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Volume 2

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Volume 2

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EDITED BY

SIR WILLIAM LAWRENCE BRAGG,
C.H., O.B.E., M.C., F.R.S., M.A. (Cantab)

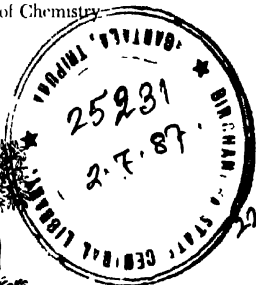
Professor Emeritus and formerly Director of the
Royal Institution of Great Britain and Fullerian Professor of Chemistry

AND

PROFESSOR GEORGE PORTER,
F.R.S., M.A., Sc.D. (Cantab)

Director of the Royal Institution of Great Britain and
Fullerian Professor of Chemistry

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Friday, January 19, 1866.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

JOHN TYNDALL, Esq. LL.D. F.R.S.

Professor of Natural Philosophy, R.I.

*On Radiation and Absorption with reference to the Colour of Bodies
and their State of Aggregation.*

THE speaker referred to the relation subsisting between the sensible phenomena of nature, and those processes lying beyond the range of the senses, on which the phenomena immediately depend. He spoke of the function of the imagination in picturing operations, which though great in their aggregate results beyond all conception, are too minute individually to be capable of observation. He referred to the luminiferous ether that fills space as the most striking illustration hitherto known of the production of a line of thought from the domain of the senses into that of the imagination, and affirmed the existence of this wonderful medium to be based upon proofs at least as strong as those which sustain the theory of gravitation.

Dwelling briefly on the relation of this ether to the atoms and molecules which are plunged in it, he illustrated, by reference to the phenomena of sound, the difference between good and bad radiators. A naked tuning-fork vibrating in free air imparted so small an amount of motion to the air that it ceased to be heard as sound at an inconsiderable distance; the same tuning-fork brought into union with its resonant case produced a sound which could be heard by thousands at once. The naked fork was a bad radiator, the combined fork and case was a powerful radiator. This combination of the fork and its case, as regards sound, roughly represented the influence of chemical combination as regards radiant heat. By the act of combination the power of the combining atoms as radiators might be augmented ten thousand-fold. As an example of this the vapour of water was selected; and it was affirmed that a pound of this vapour taken to the top of a high mountain, there heated and exposed before the cloudless heaven, would radiate nine or ten thousand times—possibly twenty thousand times—as much heat into stellar space as could be radiated by either of the constituents of the vapour when uncombined.

The speaker also referred to the well-known analogy between the pitch of a sound and the colour of light, and throwing a large spectrum upon a white screen mentioned the relation between the various colours to the rapidity of ethereal vibration. The space from the red to the blue embraced an infinite number of rates of vibration, gradually and continuously shortening without any interruption. It might be typified by an infinite number of tuning-forks of gradually augmenting pitch, and all sounding at the same time. This spectrum was derived from the carbon points of the electric light; but it was shown that in the case of various other incandescent substances the spectrum was not of this continuous character. The magnificent stream of green light produced by the volatilization of silver in the electric lamp was shown upon a screen, and afterwards the light was analyzed and found to produce two bands of brilliant green, differing but slightly from each other in refrangibility. Here the case is typified, not by an infinite number of tuning-forks, but by two tuning-forks of slightly different pitch. And just as the rate of vibration in the case of the tuning-fork is a fixed rate, so the rate of vibration of the atoms of silver vapour were fixed. And as the colour of the vapour depended on its rate of atomic vibration, the constancy of this rate secured the constancy of colour in the vapour. We cannot make the vapour of silver *white hot*, however we may exalt its temperature. We may augment the brilliancy of the particular rays that it emits, but we cannot cause it to emit that variety of rays the blending of which together produces the impression of white.

Like the vapour of silver the vapour of water has also its definite periods of vibration; and they are not such as to enable the vapour, however high its temperature may be raised, to emit a white light. It can hardly be said to emit any light at all. The flame of hydrogen, for example, is composed of intensely heated aqueous vapour, but it is hardly visible; and it is easy to give the vapour of water a temperature sufficient to raise a solid body placed in the vapour to a bright red heat, while the vapour itself remains absolutely dark. Now the powers of radiation and absorption go hand in hand, and the body which cannot emit luminous rays is incompetent to absorb them. Thus the sun's luminous rays pass freely through the aqueous vapour of our atmosphere; while it is the impediment offered by this same vapour to the radiation from the earth which checks the sudden drain of terrestrial heat, and thus renders our planet inhabitable.

This power of electric absorption was illustrated by the action of two tuning-forks which sounded the same note. Both forks being mounted on their resonant stands, one of them was first sounded. The silent fork was then brought near the sounding one, and held near it for five seconds. The vibrations of the excited fork were then quenched, but the sound did not cease to be heard. In fact the silent fork had taken up the vibrations of its neighbour, and continued to sound after the latter had ceased to vibrate. Again, one fork being permitted to remain upon its stand, the other was dismounted and

thrown into strong vibration. Detached from its stand, its sound was too feeble to be heard by the audience ; but on bringing it near the mounted fork a mellow sound rose which filled the room. Thus the vibrations of the one fork were transmitted through the air and imparted to the other. To effect this transference it was necessary that the forks should be in perfect unison : the fixing upon either of them of a bit of wax not larger than a pea was sufficient to destroy the power of the forks to influence each other.

Thus one sounding body absorbs the vibration of another sounding body with which it is in unison ; and here we have in acoustics the representative of that great principle which in optics lies at the base of spectrum analysis, namely, that bodies absorb those rays which they can themselves emit. Thus green vapour of silver if interposed in the path of a beam of white light, will absorb the green which it can itself emit. Thus also the incandescent vapour of sodium, itself intensely yellow, cuts clearly out the yellow band of the spectrum. And the same is true of aqueous vapour. Its periods of vibration synchronize with those of the rays, or more accurately *waves*, emitted by the warmed earth, and hence its power to intercept those waves by taking up their motion. But it is in dissonance with the luminous waves emitted by the sun, and hence those waves pass through large quantities of it with scarcely sensible absorption.

This incompetence of aqueous vapours to absorb luminous rays is shared by all really transparent bodies ; in fact, they are transparent in virtue of their incapacity to absorb luminous rays. Now, transparent bodies in a state of powder are always white, and in white bodies luminous rays have no power. The *light* of the sun, for example, cannot warm white sugar, nor can it warm table salt, nor flour, nor a white dress ; it cannot even melt snow. The most powerful luminous beam may be concentrated upon a surface covered with hoar frost without melting a single spicula of the frost crystals. How, then, it may be asked, does sunshine clear away the snow from the mountain heads ? Two or three days' sunshine on the mountains suffices to obliterate the traces of a heavy snow-fall : how can this occur if sunshine has no power to melt the snow crystals ? It is not the luminous rays of the sun which perform this work, but a body of rays which, though possessing high calorific power, have no light in them. By a process of transmutation these dark rays may be converted into luminous ones, but as they come from the sun, and fall upon the mountain summits, they are utterly incompetent to excite vision. Every stream which channels the glaciers or tumbles down the valleys of the Alps is the direct product of this invisible radiation. To it also the glaciers owe their birth as well as their dissolution. For while the luminous rays of the sun falling on the tropical ocean penetrate the water to great depths without considerable absorption, the dark rays are in great part absorbed close to the surface of the ocean ; they therefore heat the water at the surface, and are thus almost the sole excitants of evaporation. Not only, then, do those invisible solar rays, by the

fusion of the ice, give birth to the rivers of Switzerland, but it is they that lift the material of these rivers from the sea and store it on the frozen summits of the mountains.

Gathering up the rays emitted by a powerful electric lamp, and concentrating them upon a small focus, water, alcohol, or ether placed at the focus speedily boils, some of them, indeed, almost instantly. But they are not boiled by the luminous rays, though these produce an impression too dazzling to be borne upon the eye. Interposing in the path of the concentrated beam a glass cell containing pure distilled water, the light of the beam is not sensibly diminished, but it is no longer competent to boil or even heat water at the focus. Placing a piece of ice at the luminous focus it is not melted, though, if blackened wood be placed there, it is set on fire. The moment, however, the cell of water is withdrawn the ice melts—melts because the dark rays previously absorbed by the water of the cell are now absorbed by it. There are liquids of very low boiling points—bisulphide of carbon, for instance—which, when placed at the focus where the whole radiation, dark and bright, of the electric lamp is converged, cannot be caused to boil, can hardly be warmed. Water, for instance, requires a temperature of 212° Fahr. to boil it, bisulphide of carbon requires only $118^{\circ} 4'$; still the former is boiled in a time insufficient to warm the latter. This arises from the fact, that while water powerfully absorbs the dark calorific rays and allows the luminous ones free transmission, the bisulphide of carbon is transparent to both classes of rays, and hence is warmed by neither of them. Thus, also, when it was stated that sugar could not be warmed by the *light* of the sun, the invisible solar rays were meant to be excluded, for when the *total* radiation of the sun is converged upon white sugar it is immediately burnt up, the agent of its combustion being, however, the dark radiation.

It is possible to filter the composite radiation from the sun or from the electric light, so as to detach almost completely the visible from the invisible rays. It has been already stated that bisulphide of carbon is transparent to both classes of rays; now iodine, a substance which dissolves freely in the bisulphide, is eminently transparent to the invisible rays alone. Hence, a combination of these two substances furnishes us with a *ray-filter*, which, while it pitilessly cuts off the bright rays, allows the dark ones free transmission. At the dark focus we can boil water or alcohol, but we cannot warm bisulphide or bichloride of carbon. Bromine also, notwithstanding its volatility, bears exposure at the focus without being heated. Sulphur also bears the temperature of the focus for a considerable time without ignition. Common phosphorus, a combustible so quick that the warmth of the fingers when in contact with it suffices to provoke combustion, bears for twenty or thirty seconds without ignition the action of *radiant heat* at a focus where, in the fraction of a second, platinized platinum is raised to a white heat. The phosphorus is in a great degree transparent to radiant heat. The red iodide of mercury strewn on paper and exposed at the focus has its colour discharged where the invisible images of the carbon points fall

upon it, but owing to the transparency of the iodide to radiant heat, it requires some exposure to produce the thermograph. This red substance is far less absorbent of radiant heat than white paper, and hence it is sometimes easier to obtain a thermograph of the carbon points by exposing to the radiation from the lamp the *back* of the paper on which the iodide is strewn, than by exposing the face covered with the iodide. It is often, indeed, more easy to *burn* a thermograph through the paper than to discharge the colour of the iodide. Hence, white paper may be protected from radiant heat by being covered with a substance like the iodide of mercury.

We are here naturally reminded of the experiments of Franklin, which consisted in placing cloths of various colours upon snow, and observing the depth to which they sank in the snow when exposed to direct sunshine. Franklin concluded that the lighter the colour of the body the less is its power of absorption. The generalizations founded on this experiment are for the most part fallacious. Results long ago obtained, establishing the vast influence of chemical constitution on radiant heat, led the speaker to contrast iodine, an element, with alum, a body of highly complex character. Both substances were in powder, the one being dark, the other white. Exposed to the radiation from various sources, the white powder proved itself in all cases the most powerful absorber. The dark powder of amorphous phosphorus was also compared with the hydrated oxide of zinc, but the white powder was the best absorber. Bodies of the same colour compared together showed similar differences. The red oxide of lead for example was contrasted with the red iodide of mercury, and the oxide proved the most powerful absorber. So also the white chloride of silver was compared with the white carbonate of lead, the lead salt proved by far the most powerful absorber. In this way it was proved that as regards the absorption of radiant heat, white in some cases exceeds black, black in some cases exceeds white, and the other colours are equally capricious; all evidently depending on the chemical constitution of the substances. Here, as in other cases moreover, radiation and absorption go hand in hand, the substance which absorbs heat most powerfully radiating the same heat most copiously.

In the case of Franklin's white cloth exposed on snow to sunshine, there is no reason why it should sink at all; there is, on the contrary, reason to conclude that it must rise relatively to the snow surrounding it. For, as regards the luminous rays of the sun, they are alike powerless to warm the cloth or to melt the snow. Whatever effect is produced is therefore due to the dark solar rays. Now, snow absorbs these rays with greater greediness than any other substance; hence the white cloth, which absorbs less than the snow, really defends the snow underneath it from the action of the sun, and owing to this protection the cloth, if exposed for a sufficient time, will rise in relation to the surface round, just like a glacier table.

But though the cloth is not so good an absorber as the snow, it is nevertheless a very powerful absorber; it comes near the snow in this

respect. And when, as in the case of the black cloth, we have added to the absorption of a large portion of the dark rays by the cloth, the absorption of the whole of the luminous rays by the dye, the sum of the absorption of both classes of rays exceeds the absorption by the snow of the dark rays alone. The black cloth will therefore sink in the snow. This is the explanation of Franklin's experiment.

The speaker concluded by referring to various experiments on the transmission of radiant heat through rock salt ; to the influence of science as a means of intellectual culture ; and to the necessary defects of any system of education in which the study of nature is neglected or ignored.

[J. T.]

Friday, March 16, 1866.

SIR HENRY HOLLAND, BART. M.D. D.C.L. F.R.S. President,
in the Chair.

BALFOUR STEWART, Esq. F.R.S.

On the Existence of a Material Medium pervading Space.

THE question, whether interstellar and interplanetary space is a plenum or a vacuum, has for a long time engaged the attention of the scientific world.

As we can hold no communication with these distant regions, except through the light which reaches us, it is to this agent we must look to enable us to answer this question directly or indirectly, either from its own properties and nature, or from its faculty of revealing to us the position and motion of the heavenly bodies, or from both of these together.

This twofold aspect of the problem gives rise to the following questions :—

Question first.—Does the nature of light and radiant heat induce us to believe that space is a plenum or a vacuum?

Question second.—Is there anything in the motions of the heavenly bodies that gives us any information on this point?

These two questions comprise the observational evidence on the subject

By observational, as distinguished from experimental, we mean evidence derived from a region where we may observe what is going on, but into which we cannot transport ourselves so as to make any experiments; besides this evidence we may moreover make experiments on the surface of the earth in our laboratories, and derive from these experiments a certain amount of information bearing upon our question.

We have thus altogether three sources of evidence.

First.—Evidence derived from the nature of light and heat.

Second.—Evidence derived from the motion of the heavenly bodies.

Third.—Experiments made on the surface of the earth.

Possibly also the force of gravitation which is exercised by bodies at a distance, and the connection between solar spots and terrestrial magnetism, discovered by General Sabine, imply the existence of an interplanetary medium; but it is better to confine ourselves to light and heat, which differ from other influences in this respect. We know that light and heat travel with a certain velocity, and we can suppose, as it

were, a slice of light to be cut off half-way between the sun and the earth ; here then we have a certain amount of energy neither in the sun nor in the earth, but half-way between ; we cannot, however, at present, make any such assertion with regard to gravity or magnetic action.

To begin with the evidence derived from the nature of light and heat.

It is supposed by some (or rather perhaps it has been supposed, for the advocates of this theory are dying out) that light consists of exceedingly small particles which are projected into space by a luminous body on all sides, particles having different properties, but all of which, nevertheless, pass through interplanetary space with the same enormous velocity of 190,000 miles per second. On the other hand it is supposed that light consists in the transmission of some sort of motion of a medium pervading all space.

The difference between these two hypotheses may be explained in a very few words.

The theory of emission supposes the transit of an individual particle from the luminous body to the eye ; the theory of undulation or similar theory, on the other hand, merely supposes the progressive motion of a state of displacement between the luminous body and the eye. (Illustrated by an experiment.)

Thus, according to the former theory, each ray of light which passes between the sun and the earth is equivalent to the bodily transmission of a set of particles 90,000,000 of miles ; while, according to the theory of undulation, the greatest amount of relative displacement of the ether whose vibrations form this ray, is probably much less than the millionth of an inch.

Now, the difference between these two modes of viewing light as concerns our subject is this :—

The existence of an ethereal medium does not appear to be inseparably connected with the first theory or that of emission. The two ideas may be held and have been held together, but they do not appear to be inseparably connected ; on the other hand, if light and heat consist of the transmission of some sort of motion of a medium pervading space, we have to start at once with the hypothesis of such a medium. Hooke and Huyghens were the scientific authors of the undulatory theory of light, while Newton, on the other hand, was the great advocate of the theory of emission.

The scientific repute of Newton seems to have retarded the progress of the undulatory theory for nearly a century ; but of late years it has been revived and extended in this country by Young, whose name is inseparably connected with the Royal Institution, and in France by the illustrious Fresnel. It is only by an appeal to experiment that we can decide between the claims of these two rival theories, and we have to ask ourselves which best accords with the phenomena of optics.

First of all, if we assume the hypothesis of emission, it is not easy to conceive why the luminiferous particles discharged by so many different kinds of bodies should all pass through space with precisely the

same velocity. In order to escape from this difficulty, it was suggested by Arago that particles may be originally projected with different velocities, but that there is only one of these which is adapted to our organs of vision. This, however, is a very lame explanation, and the necessity for such explanations is one of the characteristics of a bad hypothesis. For if a theory be good, it is wonderful how many facts it will account for without any additional assumption, but a bad hypothesis requires to start an additional assumption for almost every new fact, until at length some one arises which cannot be won over by even this method, and so the hypothesis fails.

In the next place, it is difficult to conceive why particles, even although exceedingly small, moving with such enormous velocity, should not inflict on us terrific blows on account of their momentum; and it has been calculated that if the weight of a molecule of light amounted to but one grain, its momentum would equal that of a cannon ball 150 pounds in weight moving with a velocity of 1000 feet per second.

Even although a molecule of light should be many million times smaller than this, its momentum would still be sensible; and as millions of millions must enter the eye every instant from every visible point of every visible body, we should be pounded to atoms.

A good many years ago, Mr. Bennet made some experiments on this point. A slender straw was suspended horizontally by means of a spider's thread, and to one end of this lever a small piece of white paper was attached, and the whole was enclosed in an exhausted receiver of glass, while the sun's rays, concentrated by a large lens, were allowed to fall on one side of this paper; but they did not twist round the lever in the least.

The advocates of the theory of emission may perhaps, however, suppose that they are entitled to make the light molecules, and hence their momentum, as small as they choose, and of course, if this be allowed, even the most delicate experiment will not be decisive. But a short explanation will show that they are not entitled to make the momentum of a ray of light as small as they choose, but that the theory of the conservation of energy which has been elaborated by Grove, Joule, Thomson, and others, and is now universally accepted, determines this momentum.

Of course one who denies the undulatory hypothesis may, at the same time, deny the conservation of energy—we have nothing to say to such an one; but we think it can be proved that one cannot at the same time hold both the theory of emission and the theory of the conservation of energy.

In order to show this, let us suppose that such a man exists, believing the theory of the conservation of energy, but denying the undulatory hypothesis, and advocating in its stead the theory of emission. Now, in the first place, the amount of *momentum* or the *blow* which a body is capable of giving must be distinguished from the *energy* which it possesses. Thus, if we fire a rifle-bullet so as strike

an iron target (swung by a string) and lodge in it, this target or pendulum will be swung to a side on account of the momentum or blow of the ball. But as far as momentum is concerned, when a rifle is discharged, action and reaction are equal, so that the momentum of the ball is no greater than that of the recoiling rifle; and hence, if the rifle were swung, attached to another pendulum, the recoil of the rifle would produce the same effect as the ball in the first pendulum. (Illustrated by an experiment with a small cannon.)

But the ball does something more than swing the pendulum, it ultimately heats it; and, in fact, this amount of heating forms very much the energy of the ball.

Now energy is known to be proportional to the momentum or blow multiplied by the velocity, and hence it is owing to its high velocity that a rifle-ball possesses so much energy. Let us now return to Bennet's experiment, in which a powerful beam of light was made to strike a piece of paper fastened to the end of a straw, delicately suspended in the centre by a spider's thread. By the theory of the conservation of energy, we know that the energy of the light and heat which strike the paper in one minute, will, just as in the case of the rifle-ball, be represented by the whole heating effect produced.

Now we can roughly estimate this heating effect, and we can therefore find the amount of energy produced by these rays in one minute, and knowing the amount of energy, we can tell at once the *blow multiplied by the velocity* to which the energy is proportional. We therefore know the *blow multiplied by the velocity* of the light, but we also know the *velocity*; hence, dividing the first by the second, we know the blow which the light ought to produce in this arrangement, if we suppose the theory of emission to be true. By a rough calculation it may be shown that the blow ought to be sensible, but Bennet found it to be insensible, hence we argue that the theory of emission is not true.

The experiment performed by MM. Foucault and Fizeau was then described. This experiment proves that light travels slower in water than in air, and this result is also in favour of the undulatory theory, but against that of emission.

Finally it was stated, that a great number of beautiful and interesting optical experiments can be explained with the greatest ease by the theory of undulations. (Through the kindness of Professor Tyndall a selection of these was exhibited.)

All these various proofs are in favour of the undulatory theory of light, and we have therefore great reason to believe in its truth, and, believing in it, we are compelled also to believe in the existence of a material medium in which these undulations may take place.

We now come to discuss the second branch of our subject, or the evidence derived from the motions of the heavenly bodies; and as yet there is only one of these that has afforded us evidence of the existence of an ethereal medium.

In November, 1818, M. Pons, in Marseilles, discovered a comet,

which M. Encke, in Berlin, after calculating its elements, found to be identical with the comets seen in 1786, 1795, and 1805. In comparing the different observations, he immediately noticed a steady decrease in the duration of the comet's revolution. M. Encke conceived that some permanently retarding force must influence the motion of the comet; but the nature of that force would only be cleared up by continuous and very carefully conducted observations at each return. Consequently, in 1819, he called the attention of astronomers to this comet; but the whole of the subsequent observations, and the calculations founded upon them, were not discussed until forty years had elapsed. M. Encke, in his first discussion, obtained the following results:—

(a.) It is impossible by the laws of planetary motion to explain the motion of this comet.

(b.) The whole period of revolution has been shortened since the first observation in 1786 by two days and eight hours, which, in proportion to its small period of revolution (about 1210 days), is far too large an amount to ascribe it to imperfections of the observations or of the instruments.

(c.) The amount of decrease is at each revolution constantly the same, and so regularly observed at each return of the comet to its perihelion that not the least doubt now exists as to the fact itself.

(d.) The mathematical consideration of the nature of the retarding force shows it to be *entirely* a tangential force, that is, such a force as is always exerted by a medium filling space where a body is in motion; it follows, that we are led to assume the existence of a medium filling all space, and producing effects analogous to those observed on our earth. This is, says M. Encke, not an artificial assumption, but the force is immediately suggested from the nature of its effects.

An experiment made by the speaker in conjunction with Professor Tait was then described. This experiment was carried out by means of an ingenious mechanical contrivance invented and made by Mr. Beckley, of the Kew Observatory. The object of the experiment was to produce very rapid rotation in vacuo. This was accomplished by carrying a slowly revolving iron shaft up a barometer tube; at the top of this tube there was a large receiver, which might be considered analogous to the vacuum of a barometer, with the exception that it was exhausted by an air-pump, and not by the Torricellian process. In this receiver, by means of multiplying gear connected with the shaft, an aluminium disk, 13 inches in diameter and $\frac{1}{16}$ th of an inch in thickness, was made to revolve with great velocity. When it was kept for 30 seconds at the full speed of 83 revolutions in a second, this disk was found to become heated nearly 1° Fahr., and this heating was independent both of the density and chemical constitution of the residual air of the vacuum.

The disk was insulated from its bearings by a piece of ebonite, so that very little heat could be conveyed from the bearings to the disk; besides, an experiment made by artificially heating the spindle showed

that the effect observed could not be due to heating of the disk by the bearings. This heating effect, it was believed, was not due to rotation under the earth's magnetic force, nor to vibration of the disk ; but the experiment was not quite finished : in the meantime, the evidence that it could not be explained by any known cause was very considerable, so that perhaps an explanation may be sought for in a resisting medium which we cannot get rid of.

[B. S.]

Friday, June 1, 1866.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

HENRY E. ROSCOE, B.A. F.R.S.

On the Opulescence of the Atmosphere.

ON a previous occasion (May 22, 1864) the speaker explained the principles of a method by the application of which we are able to gain some knowledge of the distribution of the chemically active rays on the earth's surface, and their variation from time to time. This method depends upon the comparison of tints gained by sensitive photographic paper when exposed to daylight; and it is evident that we must define the "chemical rays" to be all those which are able to produce a darkening effect upon chloride of silver paper. In order that such a mode of measurement should be possible, it is necessary, in the first place, that paper can be prepared of a uniform degree of sensitiveness; and secondly, that the relation between the several tints and the intensity of the light necessary to produce such tints should be known. These relations have been accurately ascertained, and the method is now so far perfected that the observations can be very easily and accurately made.*

The whole apparatus needed for these experiments is contained in a small box, and all the observations for a day can be made in the course of a few minutes.

Through the kindness of Mr. Balfour Stewart, determinations of the Chemical Intensity of Total Daylight have been carried on at Kew Observatory for the past year by Mr. T. W. Baker. The mean daily intensity can be readily obtained from the separate observations, and these, when plotted out as a curve, show the daily mean intensities for the year.

Daily Mean Chemical Intensities measured at Kew, April, 1865, to April, 1866.

For April, 1865	81·2	For October, 1865	29·2
" May "	97·0	" November "	12·8
" June "	76·9	" December "	6·9
" July "	100·6	" January, 1866	13·4
" August "	82·5	" February "	21·2
" September "	110·2	" March "	32·2
In Spring, 45·9	In Summer, 91·5	In Autumn, 73·9	In Winter, 11·0
(Light of the Intensity 1 acting for 24 hours taken as 1000.)			

* See 'Phil. Trans.,' 1865, p. 605: "The Bakerian Lecture."

It is seen that the condition of the sky and weather materially influences the chemical intensity of the month—thus June, 1865, was cloudy (2 days rain; 21 days cloudy; average amount of cloud, 5·5), and the mean intensity is 76·9; whereas September was a very bright month (0 days rain; 20 days cloudy; average amount of cloud, 2·5), and the chemical intensity reached 110·2.

If we compare the mean intensities for the summer and winter solstices and the equinoxes as measured at Owen's College, Manchester, we have,—

June 21	113
March and September 21	33
December 21	4·7

The above numbers show that the increase of chemical action from December to March is not nearly so great as that from March to June. This difference cannot be attributed to the common absorption exerted by the atmosphere, but may be explained as being the necessary consequence of a peculiar absorptive action which the atmosphere effects upon the chemically active rays, and to which the name of opalescence may be given.

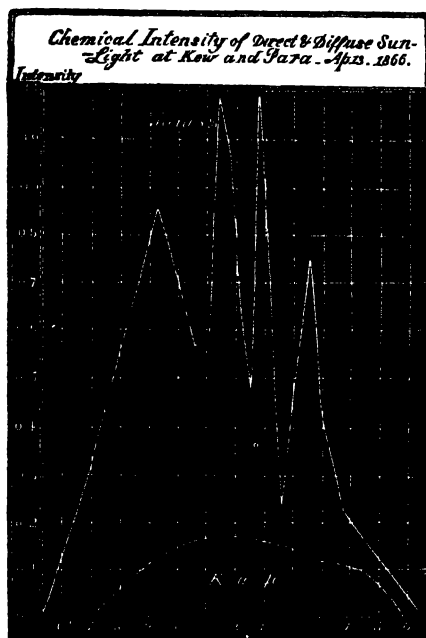
It has frequently been stated* that the chemical intensity of light on snowy peaks and in tropical climates is much less than that in our own latitudes, and that photographers in Mexico have found it impossible amidst the glaring rays of a tropical sun to obtain a picture which in the gloomy atmosphere of England would need an exposure of only one minute. In order to ascertain the degree of truth attaching to these extraordinary statements, and to obtain some insight into the chemical intensity of tropical climates, the speaker was fortunate to be able to send his assistant, Mr. T. E. Thorpe, to Pará, on the Amazons (long. 48° 30' W., and lat. 1° 28' S.). The measurements there made have already furnished some very interesting results; in the first place, we find that the daily mean chemical intensities at Pará and at Kew on the same days are represented by the following numbers:—

		Kew	Pará	
April 4, 1866	.	19·7	260·0	or as 1 to 13·1
" 7 "	.	9·3	320 0	or as 1 to 34·4
" 13 "	.	45 7	326·0	or as 1 to 7·1

The curves for these days show the enormous variation of chemical intensity which occurs under a tropical sun during the rainy season. Every afternoon regularly, and sometimes at other periods of the day, the enormous thunder-clouds discharge their contents in the form of deluging rain, and the chemical action sinks to zero; then the storm passes over, and the chemical intensity again rises (see woodcut on opposite page). It is thus seen that any difficulties which a photographer may have in the tropics cannot be ascribed to an insufficient supply of the sun's chemically active rays.

* See Golding Bird, 'Natural Philosophy,' 5th edition, p. 622.

The speaker desired, however, chiefly to direct attention this evening to some experiments which appear to throw light upon that much vexed question of the cause of the blue colour of the heavens and the ruddy tints of sunrise and sunset. Since the time of Leonardo da Vinci this subject has been a favourite ground for the display of meteorological speculations. Leonardo, and afterwards Goethe, believed that the blueness of an unclouded sky was due to the passage of the



white light through the atmosphere containing finely-divided particles. Newton explained the blue colour of the heavens by the existence in the atmosphere of hollow very minute vesicles of water, upon which, as on a soap-bubble, the colours of thin plates become perceptible; and according as the thickness of the walls of these vesicles increased, so would the colour change from blue to yellow, orange, and red; and thus, by very frequent reflections, the various tints from sky-blue to sunset-red could be explained. Founded upon this theory Clausius has calculated the relative intensities of direct sunlight and the diffuse reflected light of the sky for varying altitudes of the sun.

Some physicists have assumed that the air itself has a blue colour, whilst others have admitted that if air be of a blue colour by *reflected* light, it must appear red by *transmitted* light.

Others again, in order to avoid the difficulty of explaining the

great variety of sunset tints, have assumed these tints to be an ocular deception, or caused by the presence of clouds which receive and repeat the colour!

Many physicists have suggested that the atmosphere, being filled with small particles of floating solid matter, acts like an opalescent medium and transmits only red light; but it is to Brücke* that we are indebted for a complete statement and masterly investigation of this view of the subject. Forbes, again,† explains the phenomena in an entirely different manner; for he, observing that under certain circumstances aqueous vapour, or rather water in finely divided particles, is able to absorb the blue rays, and that the sun looked red when seen through a particular portion of a jet of escaping steam, attributes the sunset-red solely to the presence of water in this peculiar state of division.

In order to appreciate the value of these various opinions, it appears of special interest to obtain a knowledge of some quantitative facts respecting the intensity of the light transmitted directly from the sun, and that reflected by the air or particles in the atmosphere. The possibility of making such measurements with respect to those parts of the sun's light which may be expected to show great differences in reflection and transmission, viz. the most refrangible portions, is rendered at once evident by the employment of the simple method of measuring the chemical intensity of light which has been above alluded to. The method employed consists simply in determining the chemical intensity of the total daylight (sunlight and diffused light), and immediately afterwards shading off the sun's direct rays by means of a small disc or sphere of metal, whose apparent diameter is only slightly greater than that of the solar disc seen from the position of the sensitive paper. In this way the chemical intensity of the total (direct and diffused) light is compared with that given off by the whole of the heavens alone, and the difference gives the chemical intensity of the direct sunlight.

Experiment soon proved that the relative intensity of the chemical light coming directly from the sun is very much less than we should ordinarily suppose, judging from the intensity of the visible light. Thus, at Owen's College, Manchester, it was found when the sun was $12^{\circ} 3'$ above the horizon, that of 100 chemically active rays falling on the horizontal surface, less than 5 were due to the direct sunlight, whilst 95 came from the diffused light of the heavens, even when the sky was unclouded. At the same instant, of 100 rays of visible light as affecting the eye, 60 came directly from the sun, and only 40 from the diffuse sky-light. This singular result was also observed at Cheetham Hill, by Mr. Baxendell, and at Heidelberg, by Dr. Wolkoff; indeed, at this latter station, it was found on several occasions that whilst the sun was shining brightly, it was totally devoid of chemical rays, the

* 'Pogg. Ann,' vol. lxxxviii, p. 363.

† "On the Colour of Steam under certain Circumstances, and on the Colours of the Atmosphere:" 'Edin. Transactions,' xiv. p. 371; 'Phil. Mag,' xiv. xv. 3rd Series.

interposition of the small disc producing no diminution in the chemical action.

Thus, at altitudes from $0^{\circ} 34'$ to $12^{\circ} 58'$ on the following occasions, the sunlight was robbed entirely of its chemically active rays by passage through the atmosphere.

Altitude.	Direct Sun.	Diffuse Light.
$0^{\circ} 34'$	0.000	0.026
1 32	0.000	0.024
2 29	0.000	0.038
3 27	0.000	0.028
6 0	0.000	0.030
10 40	0.000	0.073
11 51	0.000	0.079
12 58	0.000	0.080

The same inactive condition of the sun at low altitudes has frequently been observed at Kew, Cheetham Hill, and Owens College.

The following numbers give the results of an extended series of observations made at Heidelberg, by Dr. Wolkoff, at Kew by Mr. Baker, at Cheetham Hill by Mr. Baxendell, at Owens College by myself, and at Pará (Brazils) by Mr. T. E. Thorpe.

The last column gives the ratio of chemical intensity of sun to sky, the fraction of the action of the diffuse light which the direct sun exerts. Thus, the ratio 0.106 at Owens College means that if 1 represents the intensity of the chemical light from the diffused light of the whole sky, 0.106 was the intensity of the ray emanated directly from the sun.

Results of Observations at Heidelberg.

	Number of Observations.	Range of Altitude of Sun	Mean Altitude of Sun.	Intensity of Sky or diffused Daylight.	Intensity of direct Sunlight	Ratio of Sun to Sky.
Group 1	10	0° to 15°	$7^{\circ} 15'$.048	.002	0.041
" 2	19	15 — 30	24 13	.131	.066	0.172
" 3	31	30 — 45	34 31	.170	.136	0.800
" 4	22	45 — 60	53 37	.174	.263	1.511
" 5	17	above 60	62 30	.199	.319	1.603

Results of Observations at Cheetham Hill.

	Number of Observations		Mean Altitude of Sun.	Intensity of Sky or diffused Daylight.	Intensity of direct Sunlight.	Ratio of Sun to Sky.
	Sky.	Sun				
Group 1	23	24	$19^{\circ} 30'$.064	.012	0.187
" 2	22	22	25 31	.091	.019	0.208
" 3	18	17	34 8	.101	.026	0.250

Results of Observations at Owens College.

	Number of Observations.		Mean Altitude of Sun.	Intensity of Sky or diffused Daylight.	Intensity of direct Sunlight.	Ratio of Sun to Sky.
	Sky.	Sun.				
Group 1	33	34	17° 8'	·066	·007	0·106
" 2	20	24	26 38	·071	·008	0·108
" 3	4	5	54 12	·140	·043	0·308

Results of Observations at Kew.

	Number of Observations.		Mean Altitude of Sun.	Intensity of Sky or diffused Daylight.	Intensity of direct Sunlight.	Ratio of Sun to Sky.
	Sky.	Sun.				
Group 1	18	18	12° 55'	0·065	0·014	0·213
" 2	8	8	21 8	0·072	0·030	0·416
" 3	7	7	28 16	0·104	0·056	0·538
" 4	6	6	41 23	0·135	0·107	0·792

Results of Observations at Pará (Brazil).

	Number of Observations.		Mean Altitude of Sun	Intensity of Sky or diffused Daylight	Intensity of Direct Sunlight.	Ratio of Sun to Sky.
	Sky.	Sun.				
Group 1	20	20	42° 21'	·451	·168	·372
" 2	25	25	62 49	·552	·277	·501
" 3	25	25	77 20	·660	·267	·401

If we compare the numbers thus obtained by experiment with those calculated by Clausius on the theory of hollow vesicles impeding the passage of the rays, we shall notice a most remarkable difference between the experimental and calculated numbers.

Ratio of Chemical Intensities of direct Sunlight to diffused Light.

Sun's Altitude.	Calculated (Clausius)	Experiments.			
		Heidelberg	Cheetham Hill.	Owens College.	Kew.
20°	0·491	0·350	0·19	0·10	0·36
25	0·896	0·180	0·20	0·11	0·47
30	1·320	0·650	0·23		0·57
35	1·690	0·820	0·26		0·65
40	2·032	1·00	—		0·75
50	2·634	1·37	—		
60	3·129	1·60	—		

Thus, whilst the theory requires that at an elevation of 20° the relation of diffuse light to sunlight was as 100 to 49·1, the experiments at Heidelberg showed a relation of 100 to 35, those of Kew of 100 to 30, at Cheetham Hill of 100 to 19, and at Owens College of 100 to 10, whilst the differences at higher altitudes

becomes still greater. The Heidelberg observations were made on the summit of the Königstuhl, at an elevation of nearly 2000 feet above the sea level, and therefore at a position beneath which a very considerable portion of the densest air was situated; when the sun attained an altitude of 40° , the direct sun's rays exert the same amount of chemical action as the diffused light of a cloudless sky. At Kew Observatory, this point of equality is not nearly reached when the altitude of the sun is 42° . At Pará, under the equator, this difference between the chemical intensity of direct and diffuse sunlight becomes even more striking, for with an altitude of 77° the ratio of direct to diffuse is less than 0.5; that is, if 100 rays come from the diffused daylight only 50 come from the direct sunlight. This is certainly a very remarkable result. We thus see that the high tropical light curves are mainly caused, not by the increase of the chemically active rays in the direct sunlight, but by the enormous increase in the chemical activity of the diffuse light. It must, however, be borne in mind, that in the Pará observations the sky was not cloudless, and much light is reflected from the heavy cumuli; it is, nevertheless, remarkable, that under a tropical sun at an altitude of 80° , the diffuse daylight, still, exert a chemical action twice as great as the direct sunlight.

That the relation between the chemically active constituents of sunlight, direct and diffused, is quite different from the relation of the visible rays, can be easily ascertained. In some of the experiments made at Chertam Hill, the shadow of a small disc was thrown on a horizontal surface of white paper, and careful estimations made of the relative brightness of the shaded and unshaded portions of the surface. A comparison of these results with those obtained at the same time for the chemical rays showed that when the sun's mean altitude was $25^\circ 16'$, the mean ratio of the chemical intensities of direct and diffuse light was 0.23 (or for 100 of diffuse light there was 23 of direct sunlight), whilst the ratio of the visible intensities was 4.0 (or for 100 of diffuse light there was 400 of direct sunlight). This shows that the action of the atmosphere was 1.74 times greater on the chemical than on the visible rays. Again, at Owens College, with a mean altitude of $12^\circ 3'$, the ratio of chemical intensity was 0.053, that of the visible intensity being 1.4; or the action of the atmosphere was 26.4 times as great upon the chemical as upon the visible rays.

How can we seek to explain this unexpected result—that the sun shining brightly, and casting a dark shadow, should at a height of 20° be capable of producing a chemical action of only $\frac{1}{10}$ th of that produced by the diffuse light from the whole of a cloudless sky?

The explanation may be rendered plain by an experiment. Let us take a very slightly milky liquid—such as water containing $\frac{1}{10}$ th grain of suspended sulphur in the gallon. So slight is the opalescence that we can scarcely detect it. Nevertheless, this minute trace of most finely-divided sulphur is sufficient to cut off the chemically active rays; the bright flash of carbonic disulphide in nitric oxide cannot explode the bulb when the opalescent solution is placed between it and the

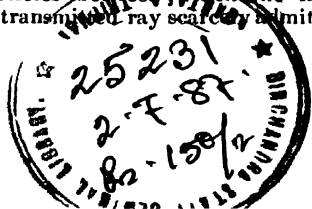
bulb; but the bulb explodes instantly when the light is allowed to pass through pure water.

We have here an exact imitation of the condition of the atmosphere as regards the chemically active rays. We see that light of a high degree of refrangibility cannot pass through the water containing the finely-divided sulphur; it is reflected back again by the particles of sulphur. So, too, the atmosphere is filled with particles which reflect the blue rays and transmit the red. What the exact nature of these particles may be, it is hard to say. We know, however, that the air is always filled with minute solid bodies. We see that in the sporules which are constantly present and cause fermentation and putrefactive decomposition. We see it also in the fact that particles of soda can always be detected in the atmosphere by spectrum-analysis. We notice these particles as motes dancing in the sunbeam, or in those grander paths of light which sometimes shoot up into the sky from a setting sun. The phenomenon may, perhaps, be caused by that finely-divided extra-terrestrial meteoric dust, which is, according to many physicists, constantly falling through the atmosphere to the earth's surface. These solid particles in the air *may* produce the above effects, and certainly do produce them; but we must remember that small particles of water are also able to transmit only red rays, and that, as Forbes has shown, the glorious ruddy tints of the setting sun are doubtless partly caused by aqueous vapour.

If the white beam of the electric lamp be passed through a tube 3 feet long, fitted with glass plates at each end, and filled with a scarcely visibly opalescent liquid, all the blue, green, and yellow rays will be completely cut off, and the immerging beam of light is deep red. Here indeed we have an artificial sunset. The finely divided sulphur reflects blue light and transmits red. If the visible light is diminished to one-third by means of opalescent sulphur, the chemically active rays are altogether cut off. The variation in the amount of this finely-divided matter, whether solid or liquid, in the air, will naturally produce variation in the tints of sunrise and sunset, and the presence at sunset of more aqueous vapour on the point of being condensed than at sunrise will explain the greater depth of colour in the setting than in the rising sun; the tints of dawn being, according to Mr. Brayley, those of evening in the reverse order.

In opal glass we have perhaps a still better illustration of the action of the atmosphere upon the chemically active rays. The opalescence of the glass is caused by the presence of very minute particles of bone-ash (calcium phosphate), or of arsenic trioxide, which are disseminated throughout the mass. By reflected light this glass appears white or bluish-white, by transmitted light it appears orange. If we place a bright source of white light behind the glass, we see that the direct rays are red, whilst the general diffused light reflected from the particles of the finely-divided matter in the glass is bluish-white.

That the size of the particles between which the light passes modifies the character of the transmitted ray scarcely admits of doubt.



This is most clearly exemplified in the beautiful phenomena of blue and ruby gold investigated by Mr. Faraday. Gold in thin plates reflects yellow, and transmits green light; but when suspended in a very fine state of division in water, it transmits blue, purple, or ruby light, according to the state of division in which it is precipitated.

The blue, purple, and ruby solutions all contain metallic gold in suspension, as Mr. Faraday has most conclusively shown, and yet they transmit totally different rays.

Hence we may fairly suppose that the varying size of the reflecting particles may aid in producing the widely differing sunset tints, from deep ruby-red to yellow and even *blue*; for we are not without several well-authenticated cases in which the sun has been seen to be *blue*. Thus, in the year 1831, a blue sun was noticed over a great part of Europe, as also in America.

We have seen that the light transmitted by finely-divided sulphur is red—it is, however, singular that blue sulphur can be formed. If we add ferric chloride to solution of sulphuretted hydrogen, we get a transient but very splendid purple tint; and we may ask ourselves whether this can be due to the size of the particle. If we heat sulphuretted hydrogen water up to 200° C. the gas decomposes, sulphur being deposited, and the solution attains a deep blue colour. Can this possibly be due to the minute division, almost approaching solution, which the sulphur attains? We find that on cooling the colour disappears, sulphur is deposited, and the liquid becomes milky. If we dissolve sulphur in sulphuric trioxide (anhydrous sulphuric acid), no chemical action that we know of occurs, and we get a magnificent deep-blue colour. Can this again be due to the minute division of the sulphur, thus permitting the blue rays alone to pass?

Finally, it is interesting to learn that both the analogues of sulphur, selenium and tellurium, yield magnificently coloured liquids when acted upon by sulphuric trioxide. Selenium in this state yields a deep olive-green solution, and tellurium a magnificent ruby-red colour.

Can these colours likewise be caused by the reflection or absorption of one kind of light and the preferential transmission of another kind by finely-divided particles?

The ruby-red gold liquid and ruby-red gold glass are both as transparent, and the one is apparently as truly a liquid as the red solution of tellurium. Yet we know that finely suspended metallic gold is the cause of this red tint. Are we acting contrary to analogy in supposing that the colour of this red liquid is caused by the particles of finely-divided tellurium, or that of these blue and green liquids by the particles of sulphur and selenium?

The speaker felt that he was here entering upon debateable ground, that, namely, of the cause of the colour of natural bodies; it was with much diffidence that he brought forward these examples of coloured solutions, and he did so only because they forced themselves on to his notice in the consideration of the plainer and now somewhat better understood phenomenon of the Opalescence of the Atmosphere.

[H. E. R.]

Friday, June 15, 1866.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

JOHN TYNDALL, Esq. LL.D. F.R.S.

PROFESSOR OF NATURAL PHILOSOPHY, R.I.

Experiments on the Vibrations of Strings.

1. I lay hold of one end of this India-rubber rope, the other end of which is fixed to the ceiling, and by a jerk raise a protuberance upon it. The protuberance runs along the rope to its fixed end, is there reflected, and reversing itself, returns to my hand. In this case, where the points of the rope rise in succession to form the protuberance, we have an example of a *progressive* wave or undulation.

2. After the first wave I now send a second, so that it shall meet the reflected wave on its return. The foremost ends of both waves now meet in the centre of the rope; they there neutralize each other, and the two halves continue to swing with an apparently motionless point called a *node* between them.

3. I now stop the rope, send a wave forward, and then another wave so quickly after it that this second wave shall meet the first at one-third of the length of the rope from its fixed end. At that point a node is produced. But I have already sent a third wave after the second. The second wave being reflected at the node, meets this third one and a second node is formed. The whole rope is now divided into three vibrating parts, separated from each other by two nodes.

4. By properly timing the impulses imparted to the rope I can divide it into four, five, six, ten, and even twenty vibrating parts, separated from each other by the appropriate number of nodes. With a certain rapidity of vibration on the part of my hand I cause the rope to swing to and fro as a whole. Twice that rapidity divides it into two equal vibrating parts; three times that rapidity into three vibrating parts, and so on. The number of vibrating parts, or *ventral segments*, as they are called, is in fact directly proportional to the rapidity of my hand's vibration.

5. In these cases, where every point of every ventral segment moves to and fro at the same time, we have examples of *stationary* undulations.

6. My hand, which produces this vibration, does not move through more than half-an-inch of space, while the ventral segments oscillate through a space of four-and-twenty. This wide vibration is

in fact produced and maintained by the addition together of small impulses properly timed. The nodes, moreover, though apparently motionless, are not strictly so; for if they were, the vibration of the segments would soon come to an end. In fact, it is by the motion transmitted through the nodes that the vibrations of the rope are sustained.

7. I might attach the free end of this rope to any suitable vibrating body instead of taking it in my hand. If the rate of vibration of the body were that of any aliquot part of the rope, it would divide itself accordingly.

8. The effect may also be produced by causing the vibrations of an aliquot part of our rope to excite vibrations in the remaining portion. Stretched vertically from top to bottom of this wooden frame is an India-rubber tube. I encircle the middle of the tube with the finger and thumb of my left hand, and pull the lower half aside with my right. The lower half vibrates, but the upper half vibrates also. In fact, the small amount of play permitted by my hand has enabled the pulse to transmit itself, to be reflected, and to accumulate its motion to this extent. I withdraw my left hand: the tube continues to vibrate in two equal parts, divided from each other by a node.

9. I encircle the tube at one-third of its length from the lower end, and pull aside the shorter segment; it vibrates more quickly than the half tube, and the vibration immediately causes the upper and longer portion to divide into two equal parts. I now withdraw my hand, and the tube continues to vibrate in three equal segments, which are separated from each other by two nodes.

10. In like manner I encircle the tube at one-quarter of its length from its lower end, and pull the lower and shorter segment aside; it vibrates, and forthwith the longer segment above divides into three vibrating parts. I now withdraw my hand, and the tube continues to oscillate in four equal segments, separated from each other by three nodes.

11. Again, from side to side of the room is stretched this stout iron wire twenty-four feet long. I seize the wire at a point which divides it into two parts, one three times as long as the other, and pulling the shorter segment aside permit it to vibrate; the remaining portion of the wire divides itself into three ventral segments. I have placed silvered beads at the nodes and at the centres of the vibrating segments; you see the light shining from those beads, and you notice that while the nodal beads remain stationary, the others describe luminous lines.

12. If I place sheets of paper across the wire at the nodes and at the ventral segments, on causing it to vibrate thus, the sheets placed across the ventral segments are tossed off, while those at the nodes remain undisturbed.

13. From these effects which you can actually see, I might pass on to vibrating strings, and show you that they divide themselves similarly. I might also show you that it is hardly possible for a

musical string to vibrate as a whole without having these smaller vibrations riding like parasites upon the large one. The addition of these smaller vibrations gives *quality* or *timbre*, or, as the Germans call it, *Klangfarbe* to the note. They constitute the harmonics of the string.

14. In this vice is fixed upright a rod of iron four feet long. I pull it aside and it vibrates as a whole; its vibrations are rendered more distinct by casting its shadow upon a white screen. I now strike the rod sharply at a point about one-third of its length from its fixed end. The pulse runs along the rod; returns from its free end, and is met by the succeeding pulses; and now the rod is divided into two vibrating parts,—a whole segment and a half segment separated from each other by this dark motionless node. By promptly striking the rod lower down, I cause it to divide into two complete vibrating segments, forming those shadowy spindles upon the screen, and half a segment at the top which spreads out like a fan. The nodes are marked by the two dark points where the shadow is complete.

15. This production of stationary undulations on a large scale through the combination of direct and reflected waves, for the illustration of which we are mainly indebted to the brothers Weber, forms a fit introduction to the experiments of M. Melde, of Marburg, who has obtained a series of very beautiful effects by associating with vibrating bodies suitably stretched strings.

16. In M. Melde's first experiment he stretched a string across a bell, or bell-jar, from edge to edge; when the bell was caused to vibrate, the string vibrated also. By varying the tension of the string it was caused to vibrate as a whole, or to divide itself into two, three, four, five or more vibrating parts, separated from each other by the appropriate number of nodes.

17. He then attached his strings to tuning-forks, and obtained the same effect in a more marked and beautiful manner. To this tuning-fork I have attached a silk string which passes round a distant peg, by turning which the string is stretched. The length of the string is eight feet. The tension at the present moment is such, that when the fork is caused to vibrate, the string swings as whole; its periods of vibration being synchronous with the impulses imparted to it by the fork. We have here a beautiful gauzy spindle produced by the silk, fully six inches wide at its point of greatest amplitude.

18. The motion of the end of the string in contact with the fork is hardly sensible, and still through this apparently motionless part of the string the whole of its motion is transmitted.

19. I relax the string by turning the peg, and now it suddenly divides itself into two ventral segments, separated from each other by a node. When the synchronism between the fork and string is perfect, the vibrations of the string are steady and long-continued; but a slight departure from synchronism introduces unsteadiness, and

the vibrations, though they may show themselves for a time, quickly disappear.

20. I relax the string still further; it now divides itself into three vibrating parts; relaxing still further, it divides into four vibrating parts; and thus I might continue to subdivide the string into ten or even twenty equal parts, separated from each other by a number of nodes one less than the number of ventral segments.

21. In the arrangement now before you, the fork vibrates in the direction of the length of the string; its tendency, therefore, is to throw the string into longitudinal vibration. But, in fact, every forward stroke of the fork raises a protuberance upon the string, which runs to its fixed end and is there reflected, so that when the longitudinal impulses are properly timed, they produce a transverse vibration. I take a heavy string in my hand, stretch it, and move my hand to and fro in the direction of the string. It vibrates as a whole, and I notice that it is always when the string is at the two limits of its excursion that my hand moves forward. If the string vibrates in a vertical plane, my hand, in order to time the impulses properly, must move forward at the moment the string reaches the upper and also at the moment it reaches the lower limit of its excursion. A little reflection will make it plain, that, in order to accomplish this, my hand must execute a complete vibration while the string executes a semi-vibration;* in other words, the vibrations of my hand must be exactly twice as rapid as those of the string.

22. Precisely the same must be true of a tuning-fork to which a proper string is attached. When the fork vibrates in the direction of the string, the number of complete vibrations which it executes in a certain time will be twice the number executed by the string.

23. If in this case the fork and string vibrate with sufficient rapidity to produce musical notes, the note of the fork will be an octave above that of the string. That it is so has been proved by M. Melde's direct observations.

24. Taking hold of the end of this heavy string, I cause my hand to move to and fro, not in the direction of the string, but at right angles to that direction. The string now swings as a whole in a vertical plane. Here every upward movement of my hand coincides with an upward movement of the string, every downward movement of my hand with a downward movement of the string. In fact, the vibrations of hand and string in this case synchronise perfectly; and if the hand could emit a musical note, the string would emit a note of the same pitch. The same holds good when a vibrating fork is substituted for

* A complete vibration, it will be borne in mind, consists of one complete excursion to and fro. A semi-vibration, on the contrary, consists of an excursion from one limit of the vibration to the other.

the vibrating hand. While, therefore, when the vibrations are longitudinal, a complete vibration of the fork synchronises with a semi-vibration of the string : when the vibrations are transversal, a complete vibration of the fork corresponds to a complete vibration of the string.

25. Hence, if the string vibrate as a whole when the vibrations are longitudinal, it will divide itself into two ventral segments when the vibrations are transversal ; or, more generally expressed, preserving the tension constant, whatever be the number of ventral segments produced by the fork when its vibrations are longitudinal, twice that number are produced when the vibrations are transverse. Here, for example, is a string eight feet long, vibrating longitudinally ; the fork divides the string into four equal vibrating parts. I place the fork so that it shall vibrate at right angles to the string. The number of ventral segments is now eight, or double the former number. This result was amply illustrated by the experiments of M. Melde.

26. Attaching two strings of the same length to the two prongs of the same fork, stretching one string in the direction of the prongs, and the other at right angles to that direction, and subjecting the strings to the same tension, when the fork is caused to vibrate, the one string divides itself into double the number of vibrating segments exhibited by the other.

27. When white silk strings vibrate thus, the beauty of the ventral segments is extreme. The nodes appear white and fixed, while the vibrating parts form delicate gauzy spindles in the air ; every protuberance of the twisted string writes its motion in a more or less luminous line on the surface of the aerial gauze.

28. Certain twisted strings do not adhere to the same plane. They vibrate simultaneously in two rectangular directions, and every one of their points describes a closed curve. When the two vibrations are of the same amplitude, and have the proper difference of phase, the ventral segments describe surfaces of revolution.

29. The path described by the various points of the string may be studied after the manner of Dr. Young, by throwing light upon them and watching the lines described by the illuminated points. By twisting a flat and burnished silver wire we form a spiral surface, from which at regular intervals the light flashes, when the whole wire is illuminated. Attaching the wire to a tuning-fork and causing it to vibrate, its luminous spots describe luminous lines. If the wire vibrate as a whole without any sensible admixture of its harmonic divisions, these spots describe straight lines which are drawn brilliantly across the ventral gauze ; but when by slackening or tightening the wire, other vibrations are caused to mingle with the fundamental one, the combination of vibrations expresses itself in luminous scrolls of extraordinary beauty.

30. But to see this beauty you must be close to it. The vibrating segments of our silk strings were, I fear, also too faint to be seen at a distance. For the silk string I substitute a fine platinum wire, which now stretches from this tuning-fork over a bridge of copper, and then round a peg. I send an electric current through the wire, which now glows brightly. I sound the fork: the wire vibrates as a whole: its two ends are brilliant, but its middle is chilled by its rapid passage through the air. Thus you have a shading off of incandescence from the ends to the centre of the wire. I relax the tension; the wire now divides itself into two vibrating parts; I relax still further and obtain three; still further, and now you have the wire divided into four, ventral segments separated from each other by these three brilliant nodes. Right and left from every node, the incandescence shades away until it disappears. You notice also that when the wire settles into steady vibration the nodes shine out more brilliantly than the wire shone before the vibration commenced. This is due to the cooling of the vibrating segments. When they are chilled by their swift passage through the air, their conductivity is improved. More electricity passes through the vibrating than through the unvibrating wire, and hence the augmented glow of the nodes.

31. Certain twisted chords, as I have said, when attached to tuning-forks execute circular instead of plane vibrations. Circular vibrations may always be obtained by attaching one end of a string to a rotating point, and timing the velocity of rotation to suit the periods of vibration possible to the string.

32. Thus, suspended from the ceiling is this white cotton rope, the lower end of which is attached to a hook belonging to this whirling table. When this handle is turned the hook rotates, describing a circle less than an inch in diameter. By properly regulating the velocity of rotation I cause the rope to divide into a series of spindles, which appear like gray gauze when projected against a dark background. I can cause the number of these spindles to vary from one to twenty by varying the velocity of rotation.

33. In this experiment the rope is vertical and the rotating wheel horizontal, but I have here an arrangement in which the wheel is vertical and the vibrating chord horizontal. Instead of a rope I now employ a burnished silver chain. Turning this wheel slowly I cause the chain to swing as a whole, and describe a spindle twelve feet long and nearly two feet in diameter at its widest part. Augmenting the speed of rotation I divide the chain into two spindles, each six feet long and more than a foot in diameter; a still higher velocity gives us three spindles, a still higher four, and so on. The gas-light here flashes at intervals from the burnished links of the chain, and each of those brilliant points describes a curve of light.

34. As soon as synchronism is established between the wheel and the chain, the amount of work performed by the arm which turns the

wheel is very sensibly augmented. Indeed it may be augmented until the strain thrown upon the chain by the accumulation of small impulses is sufficient to break it.

35. I substitute for the chain this lighter cotton-rope, round which a silver band has been coiled as a spiral; and from an electric lamp placed at the end of the rope I send a beam of light along its entire length. I now turn the wheel and divide the rope successively into two, three, four, or five ventral segments. The spindles show a graduated brilliancy, which is intensified until it becomes almost dazzling at the nodes. The vibrating chord is, indeed, better seen when the light that falls upon it has been caused to pass through coloured glass. We thus obtain at pleasure green, blue, and red spindles, with nodes like fire shading off into the more subdued light of the ventral segments.

36. Substituting for the cotton rope a string of silvered beads, twelve feet long, I send the beam from the electric lamp along the string. On every bead rests a spot of light of sunlike brilliancy. When the wheel is turned, each spot describes a circle, and every ventral segment, of which we have now four, seems formed of a series of such dazzling parallel rings, which diminish in size right and left from the points of maximum amplitude till the diameters vanish at the nodes.

37. So much for physical beauty; we have now to revert to beauty of another kind. The experiments with tuning-forks above described, may be extended to the establishment of all the laws of vibrating strings. I have here four forks, *a*, *b*, *c*, *d*, whose vibrations are in the proportion of the numbers 1, 2, 4, 8. Attaching a string eight feet long to the largest fork, I stretch it by a weight which causes it to vibrate as a whole. Keeping the stretching weight or tension the same, I attach pieces of the string to the other forks, and determine in each case the length which swings as a whole. These lengths are in the ratio of 8, 4, 2, 1.

38. *Hence the rapidity of vibration is inversely proportional to the length of the string.*

39. Here the string, eight feet long, vibrates as a whole when attached to the fork *a*. I now transfer it to *b*, still keeping it stretched by the same weight. It vibrates when *b* vibrates; but how? By dividing into two equal ventral segments. In this way alone can it accommodate itself to the vibrating period of *b*. Attached to *c*, the same string separates into four, while when attached to *d* it divides into eight ventral segments. This may be deduced immediately from the law enunciated in 38, and its experimental realization reacts as a proof of that law.

40. This result admits of extension. I have here two tuning-forks separated from each other by the musical interval called a fifth.

Attaching a string to one of the forks I stretch until it divides into two ventral segments; attached to the other fork, and stretched with the same weight, the string divides instantly into three segments when the fork is set in vibration. Now to form the interval of a fifth the vibrations of the one fork must be to those of the other in the ratio of 2 : 3. The division of the string, therefore, declares the interval. Here also are two forks separated by an interval of a fourth. With a certain tension one of the forks divides our string into three ventral segments; with the same tension the other fork divides it into four, which two numbers express the ratio of the vibrations. In the same way the division of the string in relation to all other musical intervals may be illustrated.

41. Again. Here are two tuning-forks, *a* and *b*, one of which (*a*) vibrates twice as rapidly as the other. I attach this string of silk to *a*, and stretch the string until it synchronises with the fork and vibrates as a whole. I now form a second string of silk of the same length, by laying four strands of the first side by side. I attach this compound thread to *b*, and keeping the tension the same as in the last experiment, set *b* in vibration. The compound thread synchronises with *b*, and swings as a whole. Now, by quadrupling the original thread, I obtained a string of twice the diameter of the original one: for the transverse section of any string is as the square of its diameter. Hence, as the fork *b* vibrates with half the rapidity of *a*, by doubling the diameter of the string, I halved its rapidity of vibration. In the same simple way it might be proved that by trebling the diameter of the string we reduce the number of its vibrations to one third. In general terms:—

42. *The rapidity of vibration is inversely proportional to the diameter of the string.*

43. A beautiful confirmation of this result is thus obtained:—Attached to this tuning-fork is a silk string six feet long. Two feet of this string are composed of four strands of the single thread, placed side by side, the remaining four feet are a single thread. I apply a tension, which causes the string to divide into two ventral segments. But how does it divide? Not at its centre, as is the case when the string is of uniform thickness throughout, but at the point where the thick string terminates. This thick segment, two feet long, is now vibrating at the same rate as the thin segment four feet long, a result which must manifestly follow from the combination of the two laws which we have already established. I need hardly say that if the lengths were in any other ratio than 1 : 2, the node would not be formed at the point of union of the two strings.

44. We have now to establish the third law of vibrating chords. Here are two strings of the same length and thickness. One of them is attached to the fork *b*, the other to the fork *a*, which vibrates with twice the rapidity of *b*. Stretched by a weight of 20 grains placed on this balanced scale-pan, the string attached to *b* vibrates as a whole.

Substituting the fork a for b , I find that a weight of 80 grains causes the string to vibrate as a whole. Hence to double the rapidity of vibration we must quadruple the stretching weight. In the same way it might be proved that to treble the rapidity of vibration we should have to make the stretching weight nine-fold. In general terms :—

45. *The rapidity of vibration is proportional to the square root of the tension.*

46. In the foregoing experiment both the tension and the rate of vibration were caused to vary. We will now cause the tension alone to vary, and observe the effect upon the entire string. I carry this silk chord from this tuning-fork to the scale-pan, and stretch it by a weight of 80 grains. The string vibrates as a whole. By diminishing the weight I relax the string, which finally divides sharply into two ventral segments. What is now the stretching weight? 20 grains. With a stretching weight of almost exactly 9 grains it divides into three segments, while with a stretching weight of 5 grains it divides into four segments. Thus then a tension of one-fourth doubles, a tension of one-ninth trebles, a tension of one-sixteenth quadruples the number of ventral segments. In general terms, the number of segments is inversely proportional to the square root of the tension. This result may be deduced by reasoning from the laws enunciated in 38 and 45, and its realization in fact confirms their correctness.*

47. Finally, I have here three wires of the same length and thickness, but of very different densities; one of them is of the light metal aluminium, another of silver, and another of the heavy metal platinum. I attach the wires in succession to this tuning-fork, and determine the weights necessary to cause them to vibrate as a whole, or to form the same number of ventral segments. The stretching weights here necessary I find to be directly proportional to the specific gravities of the wires. From this result, combined with that enunciated in 45, it follows that—

48. *The rapidity of vibration of different chords of the same length and thickness is inversely proportional to the square root of their densities.*

49. It is, perhaps, worth remarking that, by means of a tuning-fork, the specific gravities of all metals capable of being drawn into wires of sufficient fineness and tenacity may be determined.

The foregoing laws have been combined in various ways; and the deductions drawn from them, when subjected to the test of direct experiment, have, in every instance, been verified.

[J. T.]

* This experiment, in whole or in part, has been already performed by Prof. Foster, of University College.

Friday, January 18, 1867.

JOHN TYNDALL, Esq. LL.D. F.R.S.

PROFESSOR OF NATURAL PHILOSOPHY, R.I. ETC.

On Sounding and Sensitive Flames.

HISTORICAL.

THE sounding of a hydrogen flame when enclosed within a glass tube was, I believe, first noticed by Dr. Higgins, in 1777. The subject has been since investigated by Chladni, De la Rive, Faraday, Wheatstone, Rijke, Sondhauss, and Kundt. The action of unisonant sounds on flames enclosed in tubes has been investigated by Count Schaffgotsch and myself. The jumping of a *naked* fish-tail flame, in response to musical sounds, was first noticed by Professor Leconte at a musical party in the United States. He made the important observation that the flame did not jump until it was near *flaring*. That his discovery was not further followed up by this learned investigator was probably due to too great a stretch of courtesy on his part towards myself.* Last year, while preparing the experiments for one of my "Juvenile Lectures," my late assistant, Mr. Barrett, observed the effect independently; and he afterwards succeeded in illustrating it by some very striking experiments. With a view to the present discourse, and also to the requirements of a forthcoming work on

* The observation of Professor Leconte is thus graphically described:—"Soon after the music commenced, I observed that the flame of the last-mentioned burner exhibited pulsations in height which were *exactly synchronous* with the audible beats. This phenomenon was very striking to every one in the room, and especially so when the strong notes of the violoncello came in. It was exceedingly interesting to observe how perfectly even the *trills* of this instrument were reflected on the sheet of flame. *A deaf man might have seen the harmony.* As the evening advanced, and the diminished consumption of gas in the city *increased the pressure*, the phenomenon became more conspicuous. The *jumping* of the flame gradually increased, became somewhat irregular, and, finally it began to flare continuously, emitting the characteristic sound indicating the escape of a greater amount of gas than could be properly consumed. I then ascertained by experiment, that the phenomenon *did not* take place unless the discharge of gas was so regulated, that the flame approximated to the condition of *flaring*. I likewise determined by experiment, that the effects *were not* produced by jarring or shaking the floor and walls of the room by means of repeated concussions. Hence it is obvious that the pulsations of the flame *were not* owing to *indirect* vibrations propagated through the medium of the walls of the room to the burning apparatus, but must have been produced by the *direct* influence of aerial sonorous pulses on the burning jet."—"Phil. Mag." 4th series, vol. xv. March, 1858, p. 235; and 'Silliman's American Journal,' Jan. 1858.

Sound, the subject of sounding and sensitive flames has been recently submitted to examination in the Laboratory of the Royal Institution. The principal results of the inquiry are embodied in the following abstract.

ABSTRACT OF LECTURE.

Pass a steadily-burning candle rapidly through the air, you obtain an indented band of light, while an almost musical sound heard at the same time announces the rhythmic character of the motion. If, on the other hand, you blow against a candle-flame, the fluttering noise produced indicates a rhythmic action.

When a fluttering of the air is produced at the embouchure of an organ-pipe, the resonance of the pipe reinforces that particular pulse of the flutter whose period of vibration coincides with its own, and raises it to a musical sound.

When a gas-flame is introduced into an open tube of suitable length and width, the current of air passing over the flame produces such a flutter, which the resonance of the tube exalts to a musical sound.

Introducing a gas-flame into this tin tube three feet long, we obtain a rich musical note; introducing it into a tube six feet long, we obtain a note an octave deeper—the pitch of the note depending on the length of the tube. Introducing the flame into this third tube, which is fifteen feet long, the sound assumes extraordinary intensity. The vibrations which produce it are sufficiently powerful to shake the pillars, floor, seats, gallery, and the five or six hundred people who occupy the seats and gallery. The flame is sometimes extinguished by its own violence, and ends its peal by an explosion as loud as a pistol shot.

The roar of a flame in a chimney is of this character: it is a rude attempt at music.

By varying the size of the flame, these tubes may be caused to emit their harmonic sounds.

Passing from large tubes to small ones, we obtain a series of musical notes, which rise in pitch as the tube diminishes in length. This flame, surrounded by a tube $17\frac{1}{4}$ inches long, vibrates 159 times in a second, while that contained in this tube, $10\frac{1}{2}$ inches long, vibrates 717 times in a second. Owing to the intense heat of the sounding column, these numbers are greater than those corresponding to organ-pipes of the same lengths sounding in air.

The vibrations of the flame consist of a series of partial extinctions and revivals of the flame.

The singing flame appears continuous; but if the head be moved to and fro, or if an opera-glass, directed to the flame, be caused to move to and fro; or if, after the method of Wheatstone, the flame be

regarded in a mirror which is caused to rotate, the images due to the revivals of the flame are separated from each other, and form a chain of flames of great beauty.

With a longer tube and larger flame, by means of a concave mirror, I can project this chain of flames upon a screen. I first clasp my hand round the end of the tube so as to prevent the current of air which causes the flutter from passing over the flame:—the image of the flame is now steady upon the screen before you. I move the mirror to and fro, and you have this continuous luminous band: I withdraw my hand; the current of air passes over the flame, and instantly the band breaks up into a chain of images.

A position can be chosen in the tube at which the flame bursts spontaneously into song. A position may also be chosen where the flame is silent, but at which, if it could only be started, it would continue to sound. It is possible to start such a silent flame by a pitch-pipe, by the syron, or by the human voice. It is also possible to cause one flame to effect the musical ignition of another.

The sound which starts the flame must be nearly in unison with its own. Both flames must be so near unison as to produce distinct beats.

A flame may be employed to detect sonorous vibrations in air.

Thus, in front of this resonant case, which supports a large and powerful tuning-fork, I move this bright gas-flame to and fro. A continuous band of light is produced, slightly indented through the friction of the air. The fork is now sounded, and instantly this band breaks up into a series of distinct images of the flame.

Approaching the same flame, towards either end of one of our tin tubes, with the sounding flame within it, and causing it to move to and fro, the sonorous vibrations also effect the breaking up of the band of light into a chain of images.

In this glass-tube, fourteen inches long, a flame is sounding: I bring the flat flame of a fish-tail burner over the tube, the broad side of the flame being at right angles to the axis of the tube. The fish-tail flame instantly emits a musical note of the same pitch as that of the singing-flame, but of different quality. Its sound is, in fact, that of a membrane, the part of which it here plays.

Against a broad bat's-wing flame I allow a sheet of air, issuing from a thin slit, to impinge. A musical note is the consequence. The note can be produced by air or by carbonic acid; but it is produced with greater force and purity by oxygen. The pitch of the note depends on the distance of the slit from the flame.

Before you burns a bright candle-flame: I may shout, clap my hands, sound this whistle, strike this anvil with a hammer, or explode a mixture of oxygen and hydrogen. Though sonorous waves pass in each case through the air, the candle is absolutely insensible to the sound; there is no motion of the flame.

I now urge from this small blow-pipe a narrow stream of air through the flame of the candle, producing thereby an incipient flutter, and reducing the brightness of the flame. I now sound the whistle;

the flame jumps visibly. Matters may be so arranged that when the whistle sounds, the flame shall be either almost restored to its pristine brightness, or that the amount of light it still possesses shall disappear.

Before you now burns a bright flame from a fish-tail burner. I may, as before, shout, clap my hands, sound a whistle, or strike an anvil; the flame remains steady and without response. I urge against the broad face of the flame a stream of air from the blow-pipe just employed. The flame is cut in two by the stream of air. It flutters slightly, and now when the whistle is sounded the flame instantly starts. A knock on the table causes the two half-flames to unite and form for an instant a flame of the ordinary shape. By a slight variation of the experiment, the two side-flames disappear when the whistle is sounded, and a central tongue of flame is thrust forth in their stead.

Passing from a fish-tail to a bat's-wing burner, I obtain this broad steady flame. It is quite insensible to the loudest sound which would be tolerable here. The flame is fed from this gas-holder, which places a power of pressure at my disposal unattainable from the gas-pipes of the Institution. I turn on more gas; the flame enlarges, but it is still insensible to sound. I enlarge it still more, and now a slight flutter of its edge answers to the sound of the whistle. Turning on a little more gas, and sounding again, the jumping of the flame is still more distinct. Finally I turn on gas until the flame is on the point of roaring, as flames do when the pressure is too great. I now sound my whistle; the flame roars and thrusts suddenly upwards eight long quivering tongues.

I strike this distant anvil with a hammer, the flame instantly responds by thrusting forth its tongues.

Another flame is now before you. It issues from a burner, formed of ordinary gas tubing by my assistant. The flame is 18 inches long, and smokes copiously. I sound the whistle; the flame falls to a height of 9 inches, the smoke disappears, and the brilliancy of the flame is augmented.*

Here are two other flames, also issuing from burners formed by my assistant. The one of them is long, straight, and smoky; the other is short, forked, and brilliant. I sound the whistle; the long flame becomes short, forked, and brilliant; the forked flame becomes long and smoky. As regards, therefore, their response to the sonorous waves, the one of these flames is the exact complement of the other.

Here are various flat flames, ten inches high, and about three inches across at their widest part. They are purposely made forked flames. When the whistle sounds, the plane of each flame turns

* Mr. Barrett also observed the increase of light on the shortening of a flame by a musical sound; nor did the superior effect of high notes escape the attention of this acute and skillful young experimenter.

ninety degrees round, and continues in its new position as long as the whistle continues to sound.

Here again is a flame of admirable steadiness and brilliancy, issuing from a single circular orifice in a common iron nipple. I whistle, clap my hand, strike the anvil, and produce other sounds: the flame is perfectly steady. Observe the gradual change from this apathy to sensitiveness. The flame is now 4 inches high. I make its height 6 inches; it is still indifferent. I make it 10 inches; a barely perceptible quiver responds to the whistle. I make it 14 inches high, and now it jumps briskly the moment the anvil is tapped or the whistle sounded. I augment the pressure; the flame is now 16 inches long, and you observe a quivering which announces that the flame is near roaring. I increase the pressure; it now roars, and shortens at the same time to a height of 8 inches. I diminish the pressure a little; the flame is again 16 inches long, but it is on the point of roaring. It stands as it were on the brink of a precipice. *The whistle pushes it over.* Observe it shortens when the whistle sounds, exactly as it did when the pressure was in excess. The sonorous pulses, in fact, furnish the supplement of energy necessary to produce the roar and shorten the flame. This is the simple philosophy of all these sensitive flames.

The pitch of the note chosen to push the flame over the brink is not a matter of indifference. I have here a tuning-fork which vibrates 256 times in a second, emitting a clear and forcible note. It has no effect upon this flame. Here are three other forks, vibrating respectively 320, 384, and 512 times in a second. Not one of them produces the slightest impression upon the flame. But, besides their fundamental tones, these forks can be caused to sound a series of overtones of very high pitch. I sound this series of tones: the vibrations are now 1,600, 2,000, 2,400, and 3,200 per second respectively. The flame jumps in response to each of these sounds; the response to the highest tone of the series being the most prompt and energetic of all.

To the tap of a hammer upon a board the flame responds; but to the tap of the same hammer upon an anvil the response is much more brisk and animated. The reason is, that the clang of the anvil is rich in the higher tones to which the flame is most sensitive.

Here again is an inverted bell, which I cause to sound by means of a fiddle-bow, producing a powerful tone. The flame is unmoved. I bring a halfpenny into contact with the surface of the bell: the consequent rattle contains the high notes to which the flame is sensitive. It instantly shortens, flutters, and roars when the coin touches the bell.

Here is another flame, 20 inches long. I take this fiddle in my hand, and pass a bow over the three strings which emit the deepest notes. There is no response on the part of the flame. I sound the highest string: the jet instantly squats down to a tumultuous bushy flame, 8 inches long. I have here a small bell, the hammer of which

is caused to descend by clock-work. I hold it at a distance of 20 yards from the flame. The strokes follow each other in rhythmic succession, and at every stroke the flame falls from a height of 20 to a height of 8 inches.

The rapidity with which sound is propagated through air is well illustrated by these experiments. There is no sensible interval between the stroke of the bell and the shortening of the flame.

Some of these flames are of marvellous sensibility; one such is at present burning before you. It is nearly 20 inches long; but the slightest tap on a distant anvil knocks it down to 8. I shake this bunch of keys or these few copper coins in my hand: the flame responds to every tinkle. I may stand at a distance of 20 yards from this flame: the dropping of a sixpence from a height of a couple of inches into a hand already containing coin, knocks the flame down. I cannot walk across the floor without affecting the flame. The creaking of my boots sets it in violent commotion. The crumpling of a bit of paper, or the rustle of a silk dress, does the same. It is startled by the plashing of a raindrop. I speak to the flame, repeating a few lines of poetry; the flame jumps at intervals, apparently picking certain sounds from my utterance to which it can respond, while it is unaffected by others.

In our experiments downstairs we have called this the vowel flame, because the different vowel-sounds affect it differently. Vowel-sounds of the same pitch are known to be readily distinguishable. Their qualities or clang-tints are different, though they have a common fundamental tone. They differ from each other through the admixture of higher tones with the fundamental. It is the presence of these higher tones in different proportions that characterizes the vowel sounds; and it is to these same tones, and not to the fundamental one, that our flame is sensitive. I utter a loud and sonorous U, the flame remains steady; I change the sound to O, the flame quivers; I sound E, and now the flame is affected strongly. I utter the words *boot*, *boat*, and *beat* in succession. To the first there is no response; to the second, the flame starts; but by the third it is thrown into violent commotion; the sound *Ah!* is still more powerful. When the vowel sounds are analysed their constituents are found to vary in accordance with the foregoing experiments; those characterized by the sharpest overtones being the most powerful excitants of the flame. (See Helmholtz in Pogg. Annalen, vol. cviii. p. 286.)

The flame is peculiarly sensitive to the utterance of the letter S. If the most distant person in the room were to favour me with a "hiss," the flame would be instantly shivered into tumult. The utterance of the word "hush," or "puss," produces the same effect. This hissing sound contains the precise elements that most forcibly affect the flame. The gas issues from its burner with a hiss, and an external sound of this character added to that of a gas-jet already on the point of roaring is equivalent to an augmentation of pressure on the

issuing stream of gas. I hold in my hand a metal box containing compressed air. I turn the cock for a moment so as to allow a puff to escape: the flame instantly ducks down; not by any transfer of air from the box to the flame, for I stand at a distance which utterly excludes this idea; it is the *sound* of the issuing air that affects the flame. The hiss produced in one orifice precipitates the tumult at the other.*

Finally, I place this musical box on the table, and permit it to play. The flame responds like a sentient creature, curtsying to the notes to which it is sensitive.

[J. T.]

* Those who wish to repeat these experiments would do well to bear in mind, as an essential condition of complete success, that a free way should be open for the transmission of the vibrations from the flame *backwards*, through the gaspipe which feeds it. The orifices of the stopcocks near the flame ought to be as wide as possible.

Friday, January 25, 1867.

Sir HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, M.B. F.R.S.

On Mr. Graham's Recent Discoveries on the Diffusion of Gases.

I.

WHEN atmospheric air is separated from a vacuous or partially vacuous space by a septum, partition, or bag of india-rubber, some air passes through the septum into the originally vacuous space.

This space may be conveniently maintained vacuous, and any air passing into it be simultaneously withdrawn and delivered for examination, by means of Sprengel's exhaustor.

Whereas atmospheric air consists of about 21 per cent. of oxygen and 79 per cent. of nitrogen, the air transmitted through india-rubber into a vacuous space is found to contain about 40 per cent. of oxygen and 60 per cent. of nitrogen, and to have the property of re-inflaming a glowing splinter.

A transmission, therefore, takes place through the rubber septum of both constituents of the atmosphere, but there is a greater proportionate transmission of its oxygen than of its nitrogen.

Single or unmixed gases, similarly separated from a vacuous space by a septum of india-rubber, penetrate the rubber and enter the vacuous space with the following relative velocities :—

Nitrogen	1
Marsh-gas	2.15
Oxygen	2.55
Hydrogen	5.50
Carbonic acid	13.58

From these velocities the observed passage of mixed oxygen and nitrogen gases through india-rubber is deducible by calculation; and conversely, the separate velocities of oxygen and nitrogen are deducible from the transmission-results obtained with atmospheric air :—

Oxygen	21	×	2.55	=	53.55	.	.	.	40.4
Nitrogen	79	×	1	=	79.0	.	.	.	59.6
					<hr/>				<hr/>
					132.55				100.0

The constituent gases of atmospheric air not only pass through an india-rubber septum into a vacuous space, but also into a space

containing some other gas, such as hydrogen or carbonic acid, and at the relative velocities with which they enter a vacuous space; but the conditions of the experiment then become more complicated.

In the case of an india-rubber balloon filled with carbonic acid, for instance, not only are atmospheric oxygen and nitrogen gases continually entering the balloon, but carbonic acid gas is continually and very rapidly escaping from it.

Throughout the vacuum experiment, the conditions remain constant, the hyperoxygenized air being withdrawn as fast as transmitted; but in the balloon experiment, the oxygen is gradually accumulating within the balloon, whereby the conditions are constantly varying.

Eventually, by the rapid escape of carbonic acid, the proportion or pressure of oxygen in the internal mixture comes to exceed that in the external air; whereupon a reverse transmission through the balloon, of the excess of oxygen into the external air, at once begins.

II.

When ordinary coal gas is separated from a vacuous space by a septum, partition, or tube of platinum, some gas passes through the platinum septum into the originally vacuous space, as soon as, but not until, the metal is raised to the temperature of ignition.

Whereas coal-gas is a variable mixture of marsh-gas and hydrogen with several other gases and vapours, containing on the average about 45 per cent. of marsh-gas and 40 per cent. of hydrogen, the gas transmitted through ignited platinum is found to consist exclusively of hydrogen.

A transmission therefore of only one, and that not the most abundant of the many constituents of coal-gas, takes place into the originally vacuous space through a septum of ignited platinum.

So that while the nitrogen of the air is transmitted through a septum of india-rubber in a much smaller ratio than its oxygen, the other constituents of coal-gas are transmitted through a septum of ignited platinum in an infinitely smaller ratio than is its hydrogen.

Experimenting with single or unmixed gases, the quantity of hydrogen transmitted through a septum of ignited platinum into a vacuous space amounted to over 100 cubic centimetres in half-an-hour; whereas, under the same conditions, the quantity transmitted of oxygen, nitrogen, marsh-gas, carbonic acid, and some other gases, did not amount to .01 cubic centimetre in half-an-hour.

Further, the transmission of hydrogen through a septum of ignited platinum, as of various gases through a septum of india-rubber, takes place into a volume of some other gas as well as into a vacuum, but with a similar complication of results.

What is the nature of these transmissions of gas through india-rubber and ignited platinum respectively? Are the phenomena in

the two cases similar or dissimilar to each other; and with what class of actions are they one or both associated?

III.

By a sufficient degree of pressure, gases may be forced through the minute channels of a porous septum; or, in other words, may pass through such a septum by *transpiration*.

But transpiration takes place only through obvious channels or pores, from which india-rubber and platinum are entirely free.

Again, transpiration through a porous septum takes place only in the direction of the preponderating total pressure; but the transmission of gas through india-rubber and ignited platinum, from one gaseous space into another, can take place in the opposite direction to that of the total pressure, and in both directions at the same time, by a sort of interchange of gases through the septum.

Moreover, the composition of a mixed gas, such as atmospheric air or coal-gas, is not altered by mere transpiration; whereas the composition of these mixed gases is greatly altered by their transmissions through india-rubber and ignited platinum respectively.

Lastly, every gas and every mixture of gases has its own special velocity of transpiration, irrelative to any other property of the gas, and irreducible to any general law. These rates are altogether different from the observed rates of transmission of the same gases through india-rubber and ignited platinum, thus:—

Oxygen	1.00
Nitrogen87
Carbonic acid73
Marsh-gas53
Hydrogen44

From these differences in the character of the phenomena, as well as from another important difference hereafter to be mentioned, it is clear that the transmission of various gases through india-rubber, and of hydrogen through platinum, is not due to transpiration.

IV.

As the channels of a porous septum become more and more minute, their resistance to the bodily transmission of gas becomes greater and greater, and the quantity of gas forced through them less and less, until at length the septum becomes absolutely impermeable to transpiration, under the particular pressure.

But such a septum, of which the individual capillary channels are so small as to offer a greater resistance, or friction, to the passage of gas through them than the available pressure can overcome, may nevertheless present a considerable aggregate of interspace, through which the proper diffusive movement of gases, due to their innate molecular mobility, may take place freely.

When any volume of gas is allowed access to a vacuous space, or to an additional gaseous space, it gradually diffuses itself throughout the space afforded it, at a rate inversely proportionate for each gas to the square root of its specific gravity.

In so far as the aggregate area of interspace available for *diffusion* is greatly diminished, by the introduction of a porous non-transpiring septum between the diffusing gas and the additional space afforded it, so is the amount of diffusion within a given time proportionably diminished; but in no other respect does the septum appear to take any part in the action; it neither promotes nor retards the diffusion, but simply allows it to take place in proportion to the aggregate area of the interspace which it affords.

The experimental determination by means of Bunsen's diffusionometer of the relative diffusion-velocities of different gases through a thin plate of compressed graphite—a septum without obvious pores and quite impermeable to transpiration—has given numbers which are almost identical with the reciprocals of the square roots of the specific gravities of the several gases:—

Hydrogen	3.80
Marsh-gas	1.34
Nitrogen	1.01
Oxygen95
Carbonic acid81

Interdiffusion of different gases takes place in proportion to their respective diffusion-velocities. Thus with air and hydrogen separated from each other by a graphite septum, for every 1 volume of air which passes into the hydrogen-space, 3.8 volumes of hydrogen pass into the air-space.

Mixed gases also diffuse away from one another according to their respective diffusion-velocities. As a result of even the small superior diffusiveness of nitrogen over that of oxygen, the proportion of oxygen in atmospheric air has been increased from 21 to 24.5 per cent., by the diffusion of nitrogen away from it, during its conveyance through several lengths of porous tobacco-pipe enclosed in a vacuous space.

The acts of gas-diffusion through porous septa and of gas-transmission through india-rubber and ignited platinum resemble each other in several points. They both take place through septa free from obvious pores; they both take place as well in the direction as against the direction of the preponderating pressure, and also in opposite directions at the same time by a sort of interchange; and they both effect an alteration in the composition of any mixed gas subjected to their operations.

But they differ altogether from one another in the relative velocities with which the gas-movements in each case are effected—the transmissions of gas through india-rubber and ignited platinum being at special rates, while the diffusions of gas through porous septa are inversely as the square roots of the specific gravities of the particular gases.

Thus the specific gravity of nitrogen being somewhat less than that of oxygen, its rate of diffusion is accordingly somewhat higher, in the proportion of 101 to 95. Hence, if the passage of air through the rubber septum were due to diffusion, the transmitted air should be rather richer in nitrogen and poorer in oxygen than the original air; whereas the transmitted air is actually found to be very much richer in oxygen and poorer in nitrogen than the original air.

Again, hydrogen having a far lower specific gravity than marsh-gas, its diffusion rate is very much higher, in the ratio of 380 to 134. Hence, taking the proportion of marsh-gas to hydrogen in coal-gas, as 1 to 1, and it is usually rather greater, if the passage of coal-gas through ignited platinum were due to diffusion, for every 380 volumes of hydrogen transmitted there should be 134 volumes of marsh-gas: but in reality no marsh-gas whatever is transmitted; so that neither with the rubber septum nor with the platinum septum are the results due to diffusion.

It is rare to have phenomena of diffusion undisturbed by phenomena of transpiration, or phenomena of transpiration undisturbed by phenomena of diffusion; but since the alteration in the composition of a mixed gas by its passage through a transpiring-diffusing septum is effected solely by diffusion, the results obtained with the rubber and platinum septa are not due to joint transpiration-diffusion.

V.

A septum may be quite free from pores of any kind or degree of minuteness, and so far be absolutely impermeable to the passage of gas through it in the form of gas, but may nevertheless permit a considerable transmission of certain gases by their prior solution or *liquefaction* in the substance of the septum.

The merest film of water, as of a soap-bubble for instance, is quite impermeable to gas as gas; but allows the ready transmission of a soluble gas, such as ammonia, through it, by reason of a prior solution or liquefaction of the ammonia in the film of water.

The film of water may be replaced by a moist membrane of any degree of thinness or thickness, with a similar result.

In this case the phenomenon consists in a solution of the gas in the moist material of the septum—in a diffusion of the liquefied gas as a liquid through the thickness of the septum—in an evaporation of the liquefied gas from the remote surface of the septum—and lastly, in a diffusion of the evaporated gas into the adjoining space.

Of the many circumstances affecting the final result, the influence of the solubility of the gas in the liquid of the septum would so far predominate over all other influences as to allow of their being left out of consideration. Whence it may be affirmed that the transmission of any gas through a film of liquid, or a moist septum, will be found proportionate to the solubility of the gas in the liquid.

But gases are absorbable not only by liquids, but also by certain solids, and especially by charcoal.

The gases absorbed by charcoal are probably liquefied in the charcoal; at any rate, the more absorbable of them occupy a bulk considerably less than if reduced to the liquid state by pressure.

All charcoal is more or less porous; but its absorption of gases is not proportionate to, or a mere physical effect of, its porosity; since other similarly porous substances do not manifest the same absorptive power; and since the absorbability by charcoal of any gas is as special a property of that gas as is its solubility in water, or alcohol.

The transmission of an absorbable gas through a septum of compact charcoal, such as the cocoa-nut charcoal used by Mr. Hunter of Belfast, which absorbs about $\frac{1}{10}$ of its volume of mercury, and 111 times its volume of ammonia, would take place in two ways.

A portion of the gas would pass through the fine pores of the charcoal as gas, by diffusion, at a rate inversely proportionate to the square root of its specific gravity; while another portion would become liquefied in the charcoal by capillary condensation, pass through the charcoal as a liquid, and evaporate from the other side, just as would a gas liquefied by solution in a moist membrane; and it is conceivable that, in some compact forms of charcoal, the transmission of gas by gaseous diffusion might be inappreciable as compared with its transmission by liquefaction and evaporation.

VI.

Whereas the mere passage of gas through a transpiring or diffusing septum takes place in thorough independence of the nature of the material of the septum, in these last considered actions the transmission takes place by virtue of a sort of chemical affinity between the gas and the material of the septum—the selective absorption of the gas by the septum being a necessary antecedent of its transmission; whence it may be said that the gas is transmitted because it is first absorbed.

Is, then, the transmission of oxygen, &c., through india-rubber, and of hydrogen through ignited platinum, effected by a process, at all allied to that of gas-liquefaction by solution or capillary condensation?

That septa of india-rubber and platinum differ from merely diffusive and transpiring septa, in effecting or allowing a selective transmission of certain gases through them, is evident; but do they first exert a selective or, in other words, a *chemical absorption* of these particular gases?

Experiment answers that they do; oxygen proving to be more than twice as absorbable by india-rubber as by water, and hydrogen proving to be fully three times as absorbable by wrought-platinum as by charcoal.

The statements of fact and interpretation contained in this abstract are based upon the investigations of Mr. Graham, spread over a long period of years; and especially upon the investigations described in his more recent memoirs 'On the Molecular Mobility of Gases' (Phil. Trans., 1863), and 'On the Absorption and Diallytic Separation of Gases by Colloid Septa' (Phil. Trans., 1866).

[W. O.]

Friday, May 17, 1867.

Sir HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, M.B. F.R.S.

On the Occlusion of Gases by Metals.

I.

THE remarkable property first observed by M. Deville, in the case of homogeneous platinum and iron, when at a red heat, of being permeable to hydrogen gas, is not by any means confined to these two metals; and has been shown by Mr. Graham to be manifested in a much greater degree by palladium, even at temperatures falling considerably short of redness.

An exhausted tube of wrought palladium, surrounded by atmospheric air, remains perfectly vacuous at a red heat; surrounded by an atmosphere of hydrogen, it remains vacuous at 100°, but allows of some transmission at 240°; while at 265°, and up to a temperature just short of redness, there is a steady and considerable passage of hydrogen to its interior, maintained vacuous by the Sprengel pump. Surrounded, under the same conditions, by coal gas, the free hydrogen of the coal gas alone finds its way into the interior of the tube, the remaining constituents of the gas being excluded by the heated palladium as effectively as, in other experiments, they are excluded by ignited platinum.

This transmission of hydrogen, through the substance of various metals, is altogether different in character from the transmission of gases in general by the physical processes of transpiration and diffusion. It is evidently dependent upon some special relationship subsisting between the particular gas and metal, and has been shown by Mr. Graham to be preceded by an absorption or occlusion of the gas in the substance of the metal.

II.

Platinum-wire, drawn from the fused and solidified metal, was heated to redness and allowed to cool slowly in a current of dry hydrogen gas. After cooling, it was exposed freely to the air for some time, and then placed in a tube of porcelain or hard glass, which was

next exhausted by the Sprengel pump. After complete exhaustion, the tube was heated to redness, when the contained platinum began and continued to give off hydrogen gas, which was delivered by the pump. The quantity of hydrogen, measured cold, amounted to 21 per cent. of the volume of the platinum-wire. That the absorption did not depend upon surface, was shown by drawing out the same wire to four times its original length, and repeating the experiment when the absorption was found not to have increased, but rather to have decreased, as it amounted only to 17 per cent.

To show the effect of texture, a similar experiment was made with spongy platinum, which was found to absorb and deliver 148 per cent. of its volume of hydrogen. Experiments were also made with ordinary wrought platinum, a particular piece of which was found to occlude in three successive experiments, 553, 493, and 383 per cent. of its volume of hydrogen, measured cold, giving a mean of 476 per cent. Thus the intermediate form of platinum, more porous than the fused, but more compact than the spongy form, was found to be the most absorptive. In round numbers, 1 volume of this platinum absorbed about 5 volumes of hydrogen which, at the temperature of the experiment, would amount to some 15 volumes. Now to compress 15 cubic centimetres, for instance, of hydrogen into the space of 1 cubic centimetre would require a pressure of 15 atmospheres. But in this experiment, the 15 cubic centimetres of hydrogen were condensed, not merely into 1 cubic centimetre of space, but into so much of 1 cubic centimetre of space as appeared to be entirely occupied by platinum, and was not really so occupied. So that assuming the pores of the wrought platinum to amount to $\frac{1}{1000}$ of its bulk, the above described condensation of the hydrogen corresponded to that producible by a pressure of 15,000 atmospheres.

To show the force, with which hydrogen was retained by platinum, another piece of the wrought metal was charged with hydrogen as before, and then heated very gradually in a vacuous tube. During exposure for an hour to 220° , not a particle of gas was evolved. At a temperature slightly below that of visible redness, there was still no gas evolved. At a temperature sufficient to soften glass (500°), 1.72 c.c. of hydrogen were collected in ten minutes; and, heated for an hour in a combustion furnace, an additional 8.20 c.c. of hydrogen were collected, making altogether 9.92 c.c., or 379 per cent. of the volume of platinum employed in the experiment. The same piece of platinum, charged with hydrogen, was kept for two months, sealed up in a glass tube, which it nearly filled. At the end of that time, the air of the tube was found to be quite free from hydrogen, showing that none had been evolved by the enclosed platinum.

The absorption of hydrogen by platinum took place at a temperature much below that necessary to cause an evolution of the evolved gas. Thus some platinum-foil was found to absorb 76 per cent. of its volume of hydrogen at 100° , and 145 per cent. of its volume at 230° .

III.

Palladium appears to be a metal altogether special in its relations to hydrogen. Foil of wrought palladium that had been maintained at a temperature not exceeding 245° , and allowed to cool slowly in a current of hydrogen, evolved, when afterwards heated in vacuo, no less than 52,600 per cent., or 526 times its volume, of the gas within a quarter of an hour. But even this comparatively low temperature was found to exceed that most favourable to gas absorption. For, maintained at a temperature between 90° and 97° for three hours, and allowed to cool down during an hour and a half, the foil absorbed 643 times its volume of hydrogen, measured cold. Even at ordinary temperatures it absorbed 376 times its volume, provided it had been recently ignited in vacuo. Palladium sponge heated to 200° in a current of hydrogen, and allowed to cool slowly, afterwards yielded no less than 686 times its volume of the gas. Now if the absorption by ignited platinum of 5 times its volume of hydrogen is difficult to realize, how much more difficult is it to realize the absorption of 5 or 6 hundred times its volume of hydrogen by moderately heated palladium? Notwithstanding the levity of the gas, this large absorption of hydrogen by palladium is sufficient to increase recognizably the apparent weight of the metal. The retention, however, of such a charge of gas is not complete, a portion of the condensed hydrogen being slowly evolved or volatilized by exposure of the charged palladium to air. The hydrogen condensed in palladium is capable of exerting those particular reducing actions, which under ordinary circumstances, are producible only when the gas is in the so-called nascent state. Thus the hydrogenized palladium quickly reduces permanganate of potassium, bleaches iodide of starch, throws down prussian blue from ferric ferriocyanide, &c. Further, the absorptive power of palladium is manifested in a varying degree upon different liquids. Thus, 1,000 volumes of palladium-foil were found to absorb 1 volume of water, $5\frac{1}{2}$ volumes of alcohol, and $1\frac{1}{2}$ volumes of ether; results showing a special selective relationship of the metal to these different liquids.

IV.

The absorption of hydrogen by ignited *copper*, in the state of wire, amounted to 30 per cent., and, in the state of sponge, to 60 per cent. *Gold*, in the form of assay cornettes, was found capable of absorbing 48 per cent. of hydrogen, 29 per cent. of carbonic oxide, 16 per cent. of carbonic anhydride, and 20 per cent. of air; but of this absorbed air, nearly the whole was nitrogen. Before charging the cornettes with the above gases, it was necessary to ignite them for some time in vacuo, in order to expel the gas they had spontaneously absorbed in the muffle. This, which may be termed the natural gas of the cornettes, amounted to 212 per cent., and consisted principally of hydrogen and carbonic oxide. *Silver*, unlike the preconsidered metals, is characterized by its preferential absorption of oxygen. In different

experiments, silver-wire heated to redness was found to absorb 74 per cent. of oxygen, and nearly 21 per cent. of hydrogen. Silver-sponge absorbed 722 per cent. of oxygen, 92 per cent. of hydrogen, 52 per cent. of carbonic anhydride, and 15 per cent. of carbonic oxide. A specimen of silver-leaf, exposed to the air at a red heat, absorbed 137 per cent. of oxygen, and 20 per cent. of nitrogen; so that while ordinary atmospheric air contains 21 per cent. of oxygen, and the air absorbed by gold only about 5 per cent., the air absorbed by silver contained no less than 85 per cent. of oxygen.

V.

Iron, though tolerably absorptive of hydrogen, is specially characterized by its absorption of carbonic oxide. Ordinary iron-wire, that had been carefully cleaned and heated in vacuo to expel its natural gas, when afterwards heated in different atmospheres, was found to absorb 46 per cent. by volume of hydrogen, and 415 per cent. of carbonic oxide. The natural gas of wrought-iron, derived from the forge in which it had been heated, proved to consist principally of carbonic oxide, and, in different experiments, ranged from 700 to 1,250 per cent.; so that, in the course of its preparation, iron would appear to occlude upwards of 7 times its volume of carbonic oxide gas, which it carries about with it ever after. The discovery of this absorbability of carbonic oxide by iron has an important bearing upon the theory of aëriation. Carbonic oxide (C_2O_2) would appear to be actually absorbed by the substance of the iron, and then decomposed at a different temperature, into carbon (C) which, entering into combination with the iron, converts it into steel, and into carbonic anhydride (CO_2) which, escaping from the surface of the iron, gives rise to the appearance of blistering.

It became a matter of interest to determine whether sidereal iron, that is to say the iron of meteorites, contained any, and, if any, what natural gas. Accordingly, some 45 grammes, or 6 cubic centimetres, of meteoric iron from the Lenarto fall were heated in vacuo for two hours and a half, and found by Mr. Graham to give off 16.5 cubic centimetres of gas, which consisted substantially, not of carbonic oxide, but of hydrogen, to the extent at least of 85.5 per cent. of the entire yield of gas, the remainder being chiefly nitrogen and carbonic oxide. The inference that the meteorite, at some time or other, had been ignited in an atmosphere of which the prevailing constituent was hydrogen, is obvious; and, judging from the volume of gas yielded, the hydrogen atmosphere must have been a highly condensed one. For even under ordinary atmospheric pressure, telluric iron is found to absorb but somewhat less than half its volume; whereas this sidereal iron furnished fully two and a half times its volume of hydrogen. It is known that Father Secchi, in his classification of the stars according to their spectra, has distinguished one class, typified by α Lyrae, as having a spectrum which is essentially that of hydrogen.

VI.

In the year 1823, Mr. Faraday established the general proposition that a gas is nothing else than the vapour of a volatile liquid existing at a temperature considerably above the boiling point of the liquid; and that the condensing points of different gases are merely the boiling points of the liquids producing them. But the boiling point of a liquid, or the condensing point of its gas, is well known to be not a fixed point of temperature, but a point varying with the pressure to which the gas or liquid is subjected. Accordingly, every one of the many different gases known to chemists, with about six exceptions, has been actually condensed into the liquid state by a sufficient increase of pressure; whereby the existing temperature of the gas has ceased to be above the heightened condensing point, or boiling point, corresponding to the increased pressure. And since a gas cannot be reduced by pressure to a bulk less than that corresponding to the pressure necessary to liquefy it, without its becoming liquefied, conversely, the reduction of any gas to a bulk less than that corresponding to the pressure necessary to liquefy it, must be taken as evidence of its liquefaction. Hence, from the extremely minute volume which oxygen, hydrogen, and carbonic oxide occupy, when occluded for instance in silver, platinum, and iron respectively, there can be little doubt but that these gases, though included among the half dozen which have never been liquefied by direct pressure, do nevertheless exist in the liquid state when occluded in the above metals; or, at any rate, do not exist in the gaseous state.

As regards the nature of this absorption and presumable liquefaction of gases by metals, there are facts which seem to indicate that the phenomenon is related, on the one hand, to the absorption of gases by their solution in liquids, or in those soft solids which Mr. Graham has denominated colloids; and, on the other hand, to the absorption of gases by their condensation in the minute pores of hard solids, such as compact charcoal.

[W. O.]

Fridays, January 17 and 24, 1868.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

JOHN TYNDALL, Esq. LL.D. F.R.S.

PROFESSOR OF NATURAL PHILOSOPHY, ROYAL INSTITUTION.

On Faraday as a Discoverer.

*Parentage : Introduction to the Royal Institution : Earliest Experiments :
First Royal Society Paper : Marriage.*

It has been thought desirable to give you and the world some image of MICHAEL FARADAY, as a scientific investigator and discoverer. The attempt to respond to this desire has been to me a labour of difficulty, if also a labour of love. For however well acquainted I may be with the researches and discoveries of that great master,—however numerous the illustrations which occur to me of the loftiness of Faraday's character and the beauty of his life,—still to grasp him and his researches as a whole; to seize upon the ideas which guided him, and connected them; to gain entrance into that strong and active brain, and read from it the riddle of the world—this is a work not easy of performance, and all but impossible amid the distraction of duties of another kind. That I should at one period or another speak to you regarding Faraday and his work, is natural, if not inevitable; but I did not expect to be called upon to speak so soon. Still the bare suggestion that this is the fit and proper time for speech sent me immediately to my task: from it I have returned with such results as I could gather, and also with the wish that those results were more worthy than they are of the greatness of my theme.

It is not my intention to lay before you a *life* of Faraday in the ordinary acceptation of the term. The duty I have to perform is to give you some notion of what he has done in the world; dwelling incidentally on the spirit in which his work was executed, and introducing such personal traits as may be necessary to the completion of your picture of the *philosopher*, though by no means adequate to give you a complete idea of the *man*.

The newspapers have already informed you that Michael Faraday

was born at Newington Butts, on the 22nd of September, 1791, and that he fell finally asleep at Hampton Court, on the 25th of August, 1867. Believing, as I do, in the general truth of the doctrine of hereditary transmission—sharing the opinion of Mr. Carlyle, that “a really able man never proceeded from entirely stupid parents”—I once used the privilege of my intimacy with Mr. Faraday to ask him whether his parents showed any signs of unusual ability. He could remember none. His father, I believe, was a great sufferer during the later years of his life, and this might have masked whatever intellectual power he possessed. When thirteen years old, that is to say in 1804, Faraday was apprenticed to a bookseller and bookbinder in Blandford-street, Manchester-square: here he spent eight years of his life, after which he worked as a journeyman elsewhere.

You have also heard the account of Faraday's first contact with the Royal Institution: that he was introduced by one of the members to Sir Humphry Davy's last lectures; that he took notes of those lectures, wrote them fairly out, and sent them to Davy, entreating him at the same time to enable him to quit trade, which he detested, and to pursue science, which he loved. Davy was helpful to the young man, and this should never be forgotten: he at once wrote to Faraday, and afterwards, when an opportunity occurred, made him his assistant.* Mr. Gassiot has lately favoured me with the following reminiscence of this time:—

“CLAPHAM COMMON, SURREY,
“28th November, 1867.

“MY DEAR TYNDALL,

“Sir H. Davy was accustomed to call on the late Mr. Pepys in the Poultry on his way to the London Institution, of which Pepys was one of the original managers; the latter told me that on one occasion, Sir H. Davy, showing him a letter said, ‘Pepys, what am I to do, here is a letter from a young man named Faraday; he has been attending my lectures and wants me to give him employment at the Royal Institution, *what can I do?*’ ‘Do,’ replied Pepys, ‘put him to wash bottles; if he is good for anything, he will do it directly; if he refuses, he is good for nothing.’ ‘No, no,’ replied Davy; ‘we must try him with something better than that.’ The result was, that Davy engaged him to assist in the Laboratory at *weekly* wages.

“Davy held the joint office of Professor of Chemistry, and Director of the Laboratory; he ultimately gave up the former to the late Professor Brande,

* Here is Davy's recommendation of Faraday, presented to the managers of the Royal Institution, at a meeting on the 18th of March, 1813, Charles Hatchett, Esq., in the chair:—

“Sir Humphry Davy has the honour to inform the managers that he has found a person who is desirous to occupy the situation in the Institution lately filled by William Payne. His name is Michael Faraday. He is a youth of twenty-two years of age. As far as Sir H. Davy has been able to observe or ascertain, he appears well fitted for the situation. His habits seem good; his disposition active and cheerful, and his manner intelligent. He is willing to engage himself on the same terms as given to Mr. Payne at the time of quitting the Institution.

“Resolved,—That Michael Faraday be engaged to fill the situation lately occupied by Mr. Payne, on the same terms.”

but he insisted that Faraday should be appointed Director of the Laboratory, and, as Faraday told me, this enabled him on subsequent occasions to hold a definite position in the Institution, in which he was always supported by Davy. I believe he held that office to the last.

"Believe me, my dear Tyndall, yours truly,

"Dr. Tyndall."

"J. P. GASSIOT.

From a letter written by Faraday himself soon after his appointment as Davy's assistant, I extract the following account of his introduction to the Royal Institution :—

"LONDON, Sept. 13th, 1813.

"As for myself I am absent (from home) nearly day and night except occasional calls, and it is likely shall shortly be absent entirely, but this (having nothing more to say and at the request of my mother) I will explain to you. I was formerly a bookseller and binder, but am now turned philosopher,* which happened thus :—Whilst an apprentice, I, for amusement, learnt a little chemistry and other parts of philosophy, and felt an eager desire to proceed in that way further. After being a journeyman for six months under a disagreeable master, I gave up my business, and through the interest of a Sir H. Davy, filled the situation of chemical assistant to the Royal Institution of Great Britain, in which office I now remain; and where I am constantly employed in observing the works of nature, and tracing the manner in which she directs the order and arrangement of the world. I have lately had proposals made to me by Sir Humphry Davy, to accompany him in his travels through Europe and Asia as philosophical assistant. If I go at all I expect it will be in October next—about the end, and my absence from home will perhaps be as long as three years. But as yet all is uncertain."

This account is supplemented by the following letter, written by Faraday to his friend De la Rive,† on the occasion of the death of Mrs. Marcet. The letter is dated 2nd Sept., 1858 :—

"MY DEAR FRIEND,

"Your subject interested me deeply every way; for Mrs. Marcet was a good friend to me, as she must have been to many of the human race. I entered the shop of a bookseller and bookbinder at the age of 13, in the year 1804, remained there eight years, and during the chief part of the time bound books. Now it was in those books, in the hours after work, that I found the beginning of my philosophy. There were two that especially helped me, the 'Encyclopædia Britannica,' from which I gained my first notions of electricity, and Mrs. Marcet's 'Conversations on Chemistry,' which gave me my foundation in that science.

"Do not suppose that I was a very deep thinker, or was marked as a precocious person. I was a very lively, imaginative person, and could believe in the 'Arabian Nights' as easily as in the 'Encyclopædia.' But facts were important to me, and saved me. I could trust a fact, and always cross-examined an assertion. So when I questioned Mrs. Marcet's book by such little experiments as I could find means to perform, and found it true to the

* Faraday loved this word and employed it to the last; he had an intense dislike to the modern term *physicist*.

† To whom I am indebted for a copy of the original letter.

facts as I could understand them, I felt that I had got hold of an anchor in chemical knowledge, and clung fast to it. Thence my deep veneration for Mrs. Marcet—first, as one who had conferred great personal good and pleasure on me; and then as one able to convey the truth and principle of those boundless fields of knowledge which concern natural things, to the young, untaught, and inquiring mind.

"You may imagine my delight when I came to know Mrs. Marcet personally; how often I cast my thoughts backward, delighting to connect the past and the present; how often, when sending a paper to her as a thank-offering, I thought of my first instructress, and such like thoughts will remain with me.

"I have some such thoughts even as regards *your own father*; who was, I may say, the first who personally at Geneva, and afterwards by correspondence, encouraged, and by that sustained me."

Twelve or thirteen years ago Mr. Faraday and myself quitted the Institution one evening together, to pay a visit in Baker-street. He took my arm at the door, and, pressing it to his side in his warm genial way, said, "Come, Tyndall, I will now show you something that will interest you." We walked northwards, passed the house of Mr. Babbage, which drew forth a reference to the famous evening parties once assembled there. We reached Blandford-street, and after a little looking about, he paused before a stationer's shop, and then went in. On entering the shop, his usual animation seemed doubled; he looked rapidly at everything it contained. To the left on entering was a door, through which he looked down into a little room, with a window in front facing Blandford-street. Drawing me towards him, he said eagerly, "Look there, Tyndall; that was my working-place. I bound books in that little nook." A respectable-looking woman stood behind the counter: his conversation with me was too low to be heard by her, and he now turned to the counter to buy some cards as an excuse for our being there. He asked the woman her name—her predecessor's name—his predecessor's name. "That won't do," he said, with good-humoured impatience, who was *his* predecessor?" "Mr. Riebau," she replied, and immediately added, as if suddenly recollecting herself, "He, sir, was the master of Sir Charles Faraday." "Nonsense!" he responded, "there is no such person." Great was her delight when I told her the name of her visitor; but she assured me that as soon as she saw him running about the shop, she felt—though she did not know why—that it must be "Sir Charles Faraday."

Faraday did, as you know, accompany Davy to Rome; he was re-engaged by the managers of the Royal Institution on the 15th of May, 1815. Here he made rapid progress in chemistry, and after a time was entrusted with easy analyses by Davy. In those days the Royal Institution published 'The Quarterly Journal of Science,' the precursor of our own 'Proceedings.' Faraday's first contribution to science appeared in that journal in 1816. It was an analysis of some caustic lime from Tuscany, which had been sent to Davy by the Duchess of Montrose. Between this period and 1818 various

notes and papers were published by Faraday. In 1818 he experimented upon "Sounding Flames." Professor Auguste De la Rive, father of our present excellent De la Rive, had investigated those sounding flames, and had applied to them an explanation which completely accounted for a class of sounds discovered by De la Rive himself. By a few simple and conclusive experiments Faraday proved that the explanation was insufficient. It is an epoch in the life of a young man when he finds himself correcting a person of eminence, and in Faraday's case, where its effect was to develop a modest self-trust, such an event could not fail to act profitably.

From time to time between 1818 and 1820 Faraday published scientific notes and notices of minor weight. At this time he was acquiring, not producing; working hard for his master and storing and strengthening his own mind. He assisted Mr. Brande in his lectures, and so quietly, skilfully, and modestly was his work done, that Mr. Brande's vocation at the time was pronounced "lecturing on velvet." In 1820 Faraday published a chemical paper "on two new compounds of chlorine and carbon, and on a new compound of iodine, carbon, and hydrogen." This paper was read before the Royal Society on the 21st of Dec. 1820, and it was the first of his that was honoured with a place in the 'Philosophical Transactions.'

On the 12th of June, 1821, he married, and obtained leave to bring his young wife into his rooms at the Royal Institution. There for forty-six years they lived together, occupying the suite of apartments which had been previously in the successive occupancy of Young, Davy, and Brande. At the time of her marriage Mrs. Faraday was twenty-one years of age, he being nearly thirty. Regarding this marriage I will at present limit myself to quoting an entry written in Faraday's own hand in his book of diplomas, which caught my eye while in his company some years ago. It ran thus:—

"25th January, 1847.

"Amongst these records and events, I here insert the date of one which, as a source of honour and happiness, far exceeds all the rest. We were married on the 12th of June, 1821.

"M. FARADAY."

Then follows the copy of the minutes, dated 21st May, 1821, which gave him additional rooms, and thus enabled him to bring his wife to the Royal Institution. A feature of Faraday's character which I have often noticed makes itself apparent in this entry. In his relations to his wife he added *chivalry* to affection.

Early Researches : Magnetic Rotations : Liquefaction of Gases : Heavy Glass : Charles Anderson : Contributions to Physics.

Oersted, in 1820, discovered the action of a voltaic current on a magnetic needle; and immediately afterwards the splendid intellect of Ampère succeeded in showing that every magnetic phenomenon

then known might be reduced to the mutual action of electric currents. The subject occupied all men's thoughts; and in this country Dr. Wollaston sought to convert the deflection of the needle by the current into a permanent *rotation* of the needle round the current. He also hoped to produce the reciprocal effect of causing a current to rotate round a magnet. In the early part of 1821 Wollaston attempted to realize this idea in the presence of Sir Humphry Davy in the laboratory of the Royal Institution. This was well calculated to attract Faraday's attention to the subject. He read much about it; and in the months of July, August, and September he wrote "a history of the progress of electro-magnetism," which he published in Thomson's 'Annals of Philosophy.' Soon afterwards he took up the subject of "Magnetic Rotations," and on the morning of Christmas day, 1821, he called his wife to witness for the first time the revolution of a magnetic needle round an electric current. Incidental to the "historic skotch" he repeated almost all the experiments there referred to; and these, added to his own subsequent work, made him practical master of all that was then known regarding the voltaic current. In 1821 he also touched upon a subject which subsequently received his closer attention—the vaporization of mercury at common temperatures; and immediately afterwards conducted, in company with Mr. Stodart, experiments on the alloys of steel. He was accustomed in after years to present to his friends razors formed from one of the alloys then discovered.

During Faraday's hours of liberty from other duties he took up subjects of inquiry for himself; and in the spring of 1823, thus self-prompted, he began the examination of a substance which had long been regarded as the chemical element chlorine, in a solid form, but which Sir Humphry Davy, in 1810, had proved to be a hydrate of chlorine, that is, a compound of chlorine and water. Faraday first analyzed this hydrate, and wrote out an account of its composition. This account was looked over by Davy, who suggested the heating of the hydrate under pressure in a sealed glass tube. This was done. The hydrate fused at a blood-heat, the tube became filled with a yellow atmosphere and was found to contain two liquid substances. Dr. Paris happened to enter the laboratory while Faraday was at work. Seeing the oily liquid in his tube he rallied the young chemist for his carelessness in employing soiled vessels. On filing off the end of the tube its contents exploded and the oily matter vanished. Early next morning Dr. Paris received the following note:—

"DEAR SIR,

"The *oil* you noticed yesterday turns out to be liquid chlorine.

"Yours faithfully,

"M. FARADAY." *

The gas had been liquefied by its own pressure. Faraday then tried compression with a syringe, and succeeded thus in liquefying the gas.

* Paris: 'Life of Davy,' p. 391.

To the published account of this experiment Davy added the following note:—"In desiring Mr. Faraday to expose the hydrate of chlorine in a closed glass tube, it occurred to me that one of three things would happen: that it would become fluid as a hydrate; that decomposition of water would occur; . . . or that the chlorine would separate in a fluid state." Davy, moreover, immediately applied the method of self-compressing atmospheres to the liquefaction of muriatic gas. Faraday continued the experiments and succeeded in reducing a number of gases till then deemed permanent to the liquid condition. In 1844 he returned to the subject, and considerably expanded its limits. These important investigations established the fact that gases are but the vapours of liquids possessing a very low boiling-point, and gave a sure basis to our views of molecular aggregation. The account of the first investigation was read before the Royal Society on the 10th of April, 1823, and was published, in Faraday's name, in the 'Philosophical Transactions.' The second memoir was sent to the Royal Society on the 19th of December, 1844. I may add that while he was conducting his first experiments on the liquefaction of gases, thirteen pieces of glass were on one occasion driven by an explosion into Faraday's eye.

Some small notices and papers, including the observation that glass readily changes colour in sunlight, follow here. In 1825 and 1826 Faraday published papers in the 'Philosophical Transactions' on "new compounds of carbon and hydrogen," and on "sulphonaphthalic acid." In the former of these papers he announced the discovery of Benzol, which, in the hands of modern chemists, has become the foundation of our splendid aniline dyes. But he swerved incessantly from chemistry into physics; and in 1826 we find him engaged in investigating the limits of vaporization, and showing, by exceedingly strong and apparently conclusive arguments, that even in the case of mercury such a limit exists; much more he conceived it to be certain that our atmosphere does not contain the vapour of the fixed constituents of the earth's crust. This question, I may say, is likely to remain an open one. Mr. Rankine, for example, has lately drawn attention to the odour of certain metals; whence comes this odour, if it be not from the vapour of the metal?

In 1825 Faraday became a member of a committee, to which Sir John Herschel and Mr. Dollond also belonged, appointed by the Royal Society to examine, and if possible improve, the manufacture of glass for optical purposes. Their experiments continued till 1829, when the account of them constituted the subject of a "Bakerian Lecture." This lectureship, founded in 1774 by Henry Baker, Esq., of the Strand, London, provides that every year a lecture shall be given before the Royal Society, the sum of four pounds being paid to the lecturer. The Bakerian Lecture, however, has long since passed from the region of pay to that of honour, papers of mark only being chosen for it by the council of the Society. Faraday's first Bakerian Lecture, "On the Manufacture of Glass for Optical Purposes," was delivered

at the close of 1829. It is a most elaborate and conscientious description of processes, precautions, and results: the details were so exact and so minute, and the paper consequently so long, that three successive sittings of the Royal Society were taken up by the delivery of the lecture.* This glass did not turn out to be of important practical use, but it happened afterwards to be the foundation of two of Faraday's greatest discoveries.†

The experiments here referred to, were commenced at the Falcon Glass Works, on the premises of Messrs. Green and Pellatt, but Faraday could not conveniently attend to them there. In 1827 therefore a furnace was erected in the yard of the Royal Institution; and it was at this time, and with a view of assisting him at the furnace, that Faraday engaged Sergeant Anderson, of the Royal Artillery, the respectable, truthful, and altogether trustworthy man whose appearance here is so fresh in our memories. Anderson continued to be the reverential helper of Faraday and the faithful servant of this Institution for nearly forty years.‡

In 1831 Faraday published a paper "On a peculiar class of Optical Deceptions," to which I believe the beautiful optical toy called the Chromatropes owes its origin. In the same year he published a paper on Vibrating Surfaces, in which he solved an acoustical problem which, though of extreme simplicity *when solved*, appears to have baffled many eminent men. The problem was to account for the fact that light bodies, such as the seed of lycopodium, collected at the vibrating parts of sounding plates, while sand ran to the nodal lines. Faraday showed that the light bodies were entangled in the little whirlwinds formed in the air over the places of vibration, and through which the heavier sand was readily projected. Faraday's resources as an experimentalist were so wonderful, and his delight in experiment was so great, that he

* *Viz.* November 19, December 3 and 10.

† I make the following extract from a letter from Sir John Herschel, written to me from Collingwood, on the 3rd of November, 1867:—

"I will take this opportunity to mention that I believe myself to have originated the suggestion of the employment of borate of lead for *optical* purposes. It was somewhere in the year 1822, as well as I can recollect, that I mentioned it to Sir James (then Mr.) South; and, in consequence, the trial was made in his laboratory in Blackman-street, by precipitating and working a large quantity of borate of lead, and fusing it under a muffle in a porcelain evaporating dish. A very limpid (though slightly yellow) glass resulted, the refractive index 1.8661 (which you will find set down in my table of refractive indices in my article 'Light,' *Encyclopedia Metropolitana*). It was, however, too soft for optical use as an object glass. This Faraday overcame, at least to a considerable degree, by the introduction of silica."

‡ Regarding Anderson, Faraday writes thus in 1845:—"I cannot resist the occasion that is thus offered to me of mentioning the name of Mr. Anderson, who came to me as an assistant in the glass experiments, and has remained ever since in the laboratory of the Royal Institution. He assisted me in all the researches into which I have entered since that time; and to his care, steadiness, exactitude, and faithfulness in the performance of all that has been committed to his charge, I am much indebted.—M. F."—*Exp. Researches*, vol. iii., p. 3, footnote.

sometimes almost ran into excess in this direction. I have heard him say that this paper on vibrating surfaces was too heavily laden with experiments.

Discovery of Magneto-electricity: Explanation of Arago's Magnetism of Rotation: Terrestrial Magneto-electric Induction: The Extra Current.

The work thus far referred to, though sufficient of itself to secure no mean scientific reputation, forms but the vestibule of Faraday's achievements. He had been engaged within these walls for eighteen years.* During part of the time he had drunk in knowledge from Davy, and during the remainder he continually exercised his capacity for independent inquiry. In 1831 we have him at the climax of his intellectual strength, forty years of age, stored with knowledge and full of original power. Through reading, lecturing, and experimenting, he had become thoroughly familiar with electrical science: he saw where light was needed and expansion possible. The phenomena of ordinary electric induction belonged, as it were, to the alphabet of his knowledge: he knew that under ordinary circumstances the presence of an electrified body was sufficient to excite, by induction, an unelectrified body. He knew that the wire which carried an electric current was an electrified body, and still that all attempts had failed to make it excite in other wires a state similar to its own.

What was the reason of this failure? Faraday never could work from the experiments of others, however clearly described. He knew well that from every experiment issued a kind of radiation, luminous in different degrees to different minds, and he hardly trusted himself to reason upon an experiment that he had not seen. In the autumn of 1831 he began to repeat the experiments with electric currents, which, up to that time, had produced no positive result. And here, for the sake of younger inquirers, if not for the sake of us all, it is worth while to dwell for a moment on a power which Faraday possessed in an extraordinary degree. He united vast strength with perfect flexibility. His momentum was that of a river which combines weight and directness with the ability to yield to the flexures of its bed. The intentness of his vision in any direction did not apparently diminish his power of perception in other directions; and when he attacked a subject, expecting results, he had the faculty of keeping his mind alert, so that results different from those which he expected should not escape him through pre-occupation.

He began his experiments "on the induction of electric currents" by composing a helix of two insulated wires, which were wound side by side round the same wooden cylinder. One of these wires he

* He used to say that it required twenty years of work to make a man in Physical Science; the previous period being one of infancy.

connected with a voltaic battery of ten cells, and the other with a sensitive galvanometer. When connection with the battery was made, and while the current flowed, no effect whatever was observed at the galvanometer. But he never accepted an experimental result, until he had applied to it the utmost power at his command. He raised his battery from 10 cells to 120 cells, but without avail. The current flowed calmly through the battery wire without producing, during its flow, any sensible result upon the galvanometer.

"During its flow," and this was the time when an effect was expected—but here Faraday's power of lateral vision, separating, as it were, from the line of expectation, came into play—he noticed that a feeble movement of the needle always occurred at the moment when he made contact with the battery; that the needle would afterwards return to its former position and remain quietly there, unaffected by the *flowing* current. At the moment, however, when the circuit was interrupted the needle again moved, and in a direction opposed to that observed on the completion of the circuit.

This result and others of a similar kind led him to the conclusion "that the battery current through the one wire did in reality induce a *similar* current through the other; but that it continued for an instant only, and partook more of the nature of the electric wave from a common Leyden jar than of the current from a voltaic battery." The momentary currents thus generated were called *induced currents*, while the current which generated them was called the *inducing* current. It was immediately proved that the current generated at making the circuit was always opposed in direction to its generator, while that developed on the rupture of the circuit coincided in direction with the inducing current. It appeared as if the current on its first rush through the primary wire sought a purchase in the secondary one, and, by a kind of kick, impelled backward through the latter an electric wave, which subsided as soon as the primary current was fully established.

Faraday for a time believed that the secondary wire, though quiescent when the primary current had been once established, was not in its natural condition, its return to that condition being declared by the current observed at breaking the circuit. He called this hypothetical state of the wire the *electro-tonic state*: he afterwards abandoned this hypothesis, but seemed to return to it in later life. The term *electro-tonic* is also preserved by Professor Du Bois Reymond to express a certain electric condition of the nerves, and Professor Clerk Maxwell has ably defined and illustrated the hypothesis in the tenth volume of the 'Transactions of the Cambridge Philosophical Society.'

The mere approach of a wire forming a closed curve to a second wire through which a voltaic current flowed was then shown by Faraday to be sufficient to arouse in the neutral wire an induced current, opposed in direction to the inducing current; the withdrawal of the wire also generated a current having the same direction as the

inducing current; those currents existed only during the time of approach or withdrawal, and when neither the primary nor the secondary wire was in motion, no matter how close their proximity might be, no induced current was generated.

Faraday has been called a purely inductive philosopher. A great deal of nonsense is, I fear, uttered in this land of England about induction and deduction. Some profess to befriend the one, some the other, while the real vocation of an investigator, like Faraday, consists in the incessant marriage of both. He was at this time full of the theory of Ampère, and it cannot be doubted that numbers of his experiments were executed merely to test his deductions from that theory. Starting from the discovery of Oersted, the celebrated French philosopher had shown that all the phenomena of magnetism then known might be reduced to the mutual attractions and repulsions of electric currents. Magnetism had been produced from electricity, and Faraday, who all his life long entertained a strong belief in such reciprocal actions, now attempted to effect the evolution of electricity from magnetism. Round a welded iron ring he placed two distinct coils of covered wire, causing the coils to occupy opposite halves of the ring. Connecting the ends of one of the coils with a galvanometer, he found that the moment the ring was magnetized by sending a current through *the other coil*, the galvanometer needle whirled round four or five times in succession, the action, as before, was that of a pulse which vanished immediately. On interrupting the circuit, a whirl of the needle in the opposite direction occurred. It was only during the time of magnetization or demagnetization that these effects were produced. The induced currents declared a *change* of condition only, and they vanished the moment the act of magnetization or demagnetization was complete.

The effects obtained with the welded ring were also obtained with straight bars of iron. Whether the bars were magnetized by the electric current, or were excited by the contact of permanent steel magnets, induced currents were always generated during the rise and during the subsidence of the magnetism. The use of iron was then abandoned, and the same effects obtained by merely thrusting a permanent steel magnet into a coil of wire. A rush of electricity through the coil accompanied the insertion of the magnet; an equal rush in the opposite direction accompanied its withdrawal. The precision with which Faraday describes these results, and the completeness with which he defines the boundaries of his facts, are wonderful. The magnet, for example, must not be passed quite through the coil, but only half through, for if passed wholly through, the needle is stopped as by a blow, and then he shows how this blow results from a reversal of the electric wave in the helix. He next operated with the powerful permanent magnet of the Royal Society, and obtained with it, in an exalted degree, all the foregoing phenomena.

And now he turned the light of these discoveries upon the darkest physical phenomenon of that day. Arago had discovered in 1824,

that a disk of non-magnetic metal had the power of bringing a vibrating magnetic needle suspended over it rapidly to rest; and that on causing the disk to rotate the magnetic needle rotated along with it. When both were quiescent, there was not the slightest measurable attraction or repulsion exerted between the needle and the disk; still when in motion the disk was competent to drag after it not only a light needle but a heavy magnet. The question had been probed and investigated with admirable skill by both Arago and Ampère, and Poisson had published a theoretic memoir on the subject; but no cause could be assigned for so extraordinary an action. It had also been examined in this country by two celebrated men, Mr. Babbage and Sir John Herschel; but it still remained a mystery. Faraday always recommended the suspension of judgment in cases of doubt. "I have always admired," he says, "the prudence and philosophical reserve shown by M. Arago in resisting the temptation to give a theory of the effect he had discovered, so long as he could not devise one which was perfect in its application, and in refusing to assent to the imperfect theories of others." Now, however, the time for theory had come. Faraday saw mentally the rotating disk under the operation of the magnet flooded with his induced currents; and from the known laws of interaction between currents and magnets he hoped to deduce the motion observed by Arago. That hope he realized, showing by actual experiment that when his disk rotated currents passed through it, their position and direction being such as must, in accordance with the established laws of electro-magnetic action, produce the observed rotation.

Introducing the edge of his disk between the poles of the large horseshoe magnet of the Royal Society, and connecting the axis and the edge of the disk, each by a wire with a galvanometer, he obtained when the disk was turned round a constant flow of electricity. The direction of the current was determined by the direction of the motion, the current being reversed when the rotation was reversed. He now states the law which rules the production of currents in both disks and wires, and in so doing uses for the first time a phrase which has since become famous. When iron filings are scattered over a magnet, the particles of iron arrange themselves in certain determinate lines called magnetic curves. In 1831, Faraday for the first time called these curves "lines of magnetic force;" and he showed that to produce induced currents neither approach to nor withdrawal from a magnetic source, or centre, or pole, was essential, but that it was only necessary to cut appropriately the lines of magnetic force. Faraday's first paper on magneto-electric induction, which I have here endeavoured to condense, was read before the Royal Society on the 24th of November, 1831.

On the 12th of January, 1832, he communicated to the Royal Society a second paper on Terrestrial Magneto-electric Induction, which was chosen as the Bakerian Lecture for the year. He placed a bar of iron in a coil of wire, and lifting the bar into the direction of the

dipping needle, he excited by this action a current in the coil. On reversing the bar, a current in the opposite direction rushed through the wire. The same effect was produced, when, on holding the helix in the line of dip, a bar of iron was thrust into it. Here, however, the earth acted on the coil through the intermediation of the bar of iron. He abandoned the bar and simply set a copper-plate spinning in a horizontal plane; he knew that the earth's lines of magnetic force then crossed the plate at an angle of about 70° . When the plate spun round, the lines of force were intersected and induced currents generated, which produced their proper effect when carried from the plate to the galvanometer. "When the plate was in the magnetic meridian, or in any other plane coinciding with the magnetic dip, then its rotation produced no effect upon the galvanometer."

At the suggestion of a mind fruitful in suggestions of a profound and philosophic character—I mean that of Sir John Herschel—Mr. Barlow, of Woolwich, had experimented with a rotating iron shell. Mr. Christie had also performed an elaborate series of experiments on a rotating iron disk. Both of them had found that when in rotation the body exercised a peculiar action upon the magnetic needle, deflecting it in a manner which was not observed during quiescence; but neither of them was aware at the time of the agent which produced this extraordinary deflection. They ascribed it to some change in the magnetism of the iron shell and disk.

But Faraday at once saw that his induced currents must come into play here, and he immediately obtained them from an iron disk. With a hollow brass ball, moreover, he produced the effects obtained by Mr. Barlow. Iron was in no way necessary: the only condition of success was that the rotating body should be of a character to admit of the formation of currents in its substance: it must, in other words, be a conductor of electricity. The higher the conducting power, the more copious were the currents. He now passes from his little brass globe to the globe of the earth. He plays like a magician with the earth's magnetism. He sees the invisible lines along which its magnetic action is exerted, and sweeping his wand across these lines he evokes this new power. Placing a simple loop of wire round a magnetic needle he bends its upper portion to the west: the north pole of the needle immediately swerves to the east: he bends his loop to the east, and the north pole moves to the west. Suspending a common bar magnet in a vertical position, he causes it to spin round its own axis. Its pole being connected with one end of a galvanometer wire, and its equator with the other end, electricity rushes round the galvanometer from the rotating magnet. He remarks upon the "*singular independence*" of the magnetism and the body of the magnet which carries it. The steel behaves as if it were isolated from its own magnetism.

And then his thoughts suddenly widen, and he asks himself whether the rotating earth does not generate induced currents as it turns round its axis from west to east. In his experiment with the twirling

magnet the galvanometer wire remained at rest; one portion of the circuit was in motion *relatively to another portion*. But in the case of the twirling planet the galvanometer wire would necessarily be carried along with the earth; there would be no relative motion. What must be the consequence? Take the case of a telegraph wire with its two terminal plates dipped into the earth, and suppose the wire to lie in the magnetic meridian. The ground underneath the wire is influenced like the wire itself by the earth's rotation; if a current from south to north be generated in the wire, a similar current from south to north would be generated in the earth under the wire; these currents would run against the same terminal plate, and thus neutralize each other.

This inference appears inevitable, but his profound vision perceived its possible invalidity. He saw that it was at least possible that the difference of conducting power between the earth and the wire might give one an advantage over the other, and that thus a residual or differential current might be obtained. He combined wires of different materials, and caused them to act in opposition to each other: but found the combination ineffectual. The more copious flow in the better conductor was exactly counterbalanced by the resistance of the *wire*.^{*} Still though experiment was thus emphatic he would clear his mind of all discomfort by operating on the earth itself. He went to the round lake near Kensington Palace, and stretched 480 feet of copper wire, north and south, over the lake, causing plates soldered to the wire at its ends to dip into the water. The copper wire was severed at the middle, and the severed ends connected with a galvanometer. No effect whatever was observed. But though quiescent water gave no effect, moving water might. He therefore worked at London Bridge for three days during the ebb and flow of the tide, but without any satisfactory result. Still he urges, "Theoretically it seems a necessary consequence, that where water is flowing there electric currents should be formed. If a line be imagined passing from Dover to Calais through the sea, and returning through the land, beneath the water, to Dover, it traces out a circuit of conducting matter one part of which, when the water moves up or down the channel, is cutting the magnetic curves of the earth, whilst the other is relatively at rest. . . . There is every reason to believe that currents do run in the general direction of the circuit described, either one way or the other, according as the passage of the waters is up or down the Channel." This was written before the submarine cable was thought of, and he once informed me that actual observation upon that cable had been found to be in accordance with his theoretic deduction.*

* I am indebted to a friend for the following exquisite morsel:—"A short time after the publication of Faraday's first researches in magneto-electricity, he attended the meeting of the British Association at Oxford, in 1832. On this occasion he was requested by some of the authorities to repeat the celebrated experiment of eliciting a spark from a magnet, employing for this purpose the large magnet in the

Three years subsequent to the publication of these researches, that is to say on the 29th of January, 1835, Faraday read before the Royal Society a paper "On the influence by induction of an electric current upon itself." A shock and spark of a peculiar character had been observed by a young man named William Jenkin, who must have been a youth of some scientific promise, but who, as Faraday once informed me, was dissuaded by his own father from having anything to do with science. The investigation of the fact noticed by Mr. Jenkin led Faraday to the discovery of the *extra current*, or the current induced in the *primary wire itself* at the moments of making and breaking contact, the phenomena of which he described and illustrated in the beautiful and exhaustive paper referred to.

Seven and thirty years have passed since the discovery of magneto-electricity; but, if we except the *extra current*, until quite recently nothing of moment was added to the subject. Faraday entertained the opinion that the discoverer of a great law or principle had a right to the "spoils"—this was his term—arising from its illustration; and guided by the principle he had discovered, his wonderful mind, aided by his wonderful ten fingers, overran in a single autumn this vast domain, and hardly left behind him the shred of a fact to be gathered by his successors.

And here the question may arise in some minds, What is the use of it all? The answer is, that if man's intellectual nature thirsts for knowledge, then knowledge is useful because it satisfies this thirst. If you demand practical ends, you must, I think, expand your definition of the term practical, and make it include all that elevates and enlightens the intellect, as well as all that ministers to the bodily health and comfort of men. Still, if needed, an answer of another kind might be given to the question, "What is its use?" As far as electricity has been applied for medical purposes it has been almost exclusively Faraday's electricity. You have noticed those lines of wire which cross the streets of London. It is Faraday's currents that speed from place to place through these wires. Approaching the point of Dungeness the mariner sees an unusually brilliant light, and from

Ashmolean Museum. To this he consented, and a large party assembled to witness the experiments, which, I need not say, were perfectly successful. Whilst he was repeating them a dignitary of the university entered the room, and addressing himself to Professor Daniell, who was standing near Faraday, inquired what was going on. The Professor explained to him as popularly as possible this striking result of Faraday's great discovery. The Dean listened with attention and looked earnestly at the brilliant spark, but a moment after he assumed a serious countenance and shook his head; 'I am sorry for it,' said he as he walked away; in the middle of the room he stopped for a moment and repeated, 'I am sorry for it;' then walking towards the door, when the handle was in his hand he turned round and said, 'Indeed I am sorry for it; it is putting new arms into the hands of the incendiary.' This occurred a short time after the papers had been filled with the doings of the hay-rick burners. An erroneous statement of what fell from the Dean's mouth was printed at the time in one of the Oxford papers. He is there wrongly stated to have said, 'It is putting new arms into the hands of the infidel.'

the noble *phares* of La Hève the same light flashes across the sea. These are Faraday's sparks exalted by suitable machinery to sunlike splendour. At the present moment the Board of Trade and the Brethren of the Trinity House, as well as the Commissioners of Northern Lights, are contemplating the introduction of the magneto-electric light at numerous points upon our coasts; and future generations will be able to refer to those guiding stars in answer to the question, What has been the practical use of the labours of Faraday? But I would again emphatically say that his work needs no such justification, and that if he had allowed his vision to be disturbed by considerations regarding the practical use of his discoveries, those discoveries would never have been made by him. "I have rather," he writes in 1831, "been desirous of discovering new facts and new relations dependent on magneto-electric induction, than of exalting the force of those already obtained; being assured that the latter would find their full development hereafter."

In 1817, when lecturing before a private society in London on the element chlorine, Faraday thus expresses himself with reference to this question of utility:—"Before leaving this subject, I will point out the history of this substance, as an answer to those who are in the habit of saying on every new fact, 'What is its use?' Dr. Franklin says to such, 'What is the use of an infant?' The answer of the experimentalist is, 'Endeavour to make it useful.' When Scheele discovered this substance it appeared to have no use; it was in its infancy and useless state, but having grown up to maturity, witness its powers, and see what endeavours to make it useful have done."

Points of Character.

A point highly illustrative of the character of Faraday now comes into view. He gave an account of his discovery of magneto-electricity in a letter to his friend M. Hachette, of Paris, who communicated the letter to the Academy of Sciences. The letter was translated and published; and immediately afterwards two distinguished Italian philosophers took up the subject, made numerous experiments, and published their results before the complete memoirs of Faraday had met the public eye. This evidently irritated him. He reprinted the paper of the learned Italians in the 'Philosophical Magazine,' accompanied by sharp critical notes from himself. He also wrote a letter dated Dec. 1st, 1832, to Gay Lussac, who was then one of the editors of the 'Annales de Chimie,' in which he analyzed the results of the Italian philosophers, pointing out their errors, and defending himself from what he regarded as imputations on his character. The style of this letter is unexceptionable, for Faraday could not write otherwise than as a gentleman; but the letter shows that had he willed it he could have hit hard. We have heard much of Faraday's gentleness and sweetness and tenderness. It is all true, but it is very incomplete. You cannot resolve a powerful nature into these elements, and Faraday's

character would have been less admirable than it was had it not embraced forces and tendencies to which the silky adjectives "gentle" and "tender" would by no means apply. Underneath his sweetness and gentleness was the heat of a volcano. He was a man of excitable and fiery nature; but through high self-discipline he had converted the fire into a central glow and motive power of life, instead of permitting it to waste itself in useless passion. "He that is slow to anger," saith the sage, "is greater than the mighty, and he that ruleth his own spirit than he that taketh a city." Faraday was *not* slow to anger, but he completely ruled his own spirit, and thus, though he took no cities, he captivated all hearts.

As already intimated, Faraday had contributed many of his minor papers—including his first analysis of caustic lime—to the 'Quarterly Journal of Science.' In 1832 he collected those papers and others together in a small octavo volume, labelled them, and prefaced them thus:—

"PAPERS, NOTES, NOTICES, &c., &c.,
published in octavo,
up to 1832.
M. FARADAY."

"*Papers* of mine, published in octavo, in the *Quarterly Journal of Science*, and elsewhere, since the time that Sir H. Davy encouraged me to write the analysis of caustic lime.

"Some, I think, (at this date) are good; others moderate; and some bad. But I have put *all* into the volume, because of the utility they have been of to me,—and none more than the bad,—in pointing out to me in future, or rather, after times, the faults it became me to watch and to avoid.

"As I never looked over one of my papers a year after it was written, without believing both in philosophy and manner it could have been much better done, I still hope the collection may be of great use to me.

"Aug. 18, 1832."

"M. FARADAY."

"None more than the bad!" This is a bit of Faraday's innermost nature; and as I read these words, I am almost constrained to retract what I have said regarding the fire and excitability of his character. But is he not all the more admirable, through his ability to tone down and subdue that fire and that excitability, so as to render himself able to write thus as a little child? I once took the liberty of censuring the conclusion of a letter of his to the Dean of St. Paul's. He subscribed himself "humbly yours," and I objected to the adverb. "Well, but, Tyndall," he said, "I *am* humble; and still it would be a great mistake to think that I am not also proud." This duality ran through his character. A democrat in his defiance of all authority which unfairly limited his freedom of thought, and still ready to stoop in reverence to all that was really worthy of reverence, in the customs of the world or the characters of men.

And here, as well as elsewhere, may be introduced a letter which bears upon this question of self-control, written long years subsequent to the period at which we have now arrived. I had been at Glasgow

in 1855, at a meeting of the British Association. On a certain day, I communicated a paper to the physical section, which was followed by a brisk discussion. Men of great distinction took part in it, the late Dr. Whewell among the number, and it waxed warm on both sides. I was by no means content with this discussion; and least of all with my own part in it. This discontent affected me for some days, during which I wrote to Faraday, giving him no details, but expressing in a general way my dissatisfaction. I give the following extract from his reply:—

“SYDENHAM, 6th Oct., 1855.

“MY DEAR TYNDALI,

“These great meetings, of which I think very well altogether, advance science chiefly by bringing scientific men together, and making them to know and be friends with each other; and I am sorry when that is not the effect in every part of their course. I know nothing except from what you tell me, for I have not yet looked at the reports of the proceedings; but let me, as an old man, who ought by this time to have profited by experience, say that when I was younger, I found I often misinterpreted the intentions of people, and found they did not mean what at the time I supposed they meant; and, further, that as a general rule, it was better to be a little dull of apprehension, where phrases seemed to imply pique, and quick in perception, when on the contrary they seemed to imply kindly feeling. The real truth never fails ultimately to appear; and opposing parties if wrong are sooner convinced when replied to forbearingly, than when overwhelmed. All I mean to say is, that it is better to be blind to the results of partisanship, and quick to see good will. One has more happiness in oneself, in endeavouring to follow the things that make for peace. You can hardly imagine how often I have been heated in private when opposed, as I have thought unjustly and superciliously, and yet I have striven, and succeeded I hope, in keeping down replies of the like kind. And I know I have never lost by it. I would not say all this to you did I not esteem you as a true philosopher and friend.*

“Yours, very truly,

“M. FARADAY.”

Identity of Electricities : First Researches on Electro-Chemistry.

I have already once used the word “discomfort” in reference to the occasional state of Faraday’s mind when experimenting. It was to him a discomfort to reason upon data which admitted of doubt. He hated what he called “doubtful knowledge,” and ever tended either to transfer it into the region of undoubtful knowledge, or of certain and definite ignorance. Pretence of all kinds, whether in life or in philosophy, was hateful to him. He wished to know the reality of our nescience as well as of our science. “Be one thing or the other,” he seemed to say to an unproved hypothesis; “come out as a

* Faraday would have been rejoiced to learn that, during its last meeting at Dundee, the British Association illustrated in a striking manner the function which he here describes as its principal one. In my own case, a brotherly welcome was everywhere manifested. In fact, the differences of really honourable and sane men are never beyond healing.

solid truth, or disappear as a convicted lie." After making the great discovery which I have attempted to describe, a doubt seemed to beset him as regards the identity of electricities. "Is it right," he seemed to ask, "to call this agency which I have discovered electricity at all? Are there perfectly conclusive grounds for believing that the electricity of the machine, the pile, the gymnotus and torpedo, magneto-electricity and thermo-electricity, are merely different manifestations of one and the same agent?" To answer this question to his own satisfaction, he formally reviewed the knowledge of that day. He added to it new experiments of his own, and finally decided in favour of the "Identity of Electricities." His paper upon this subject was read before the Royal Society on the 10th and 17th of January, 1833.

After he had proved to his own satisfaction the identity of electricities, he tried to compare them quantitatively together. The terms quantity and intensity, which Faraday constantly used, need a word of explanation here. He might charge a single Leyden jar by twenty turns of his machine, or he might charge a battery of ten jars by the same number of turns. The *quantity* in both cases would be sensibly the same, but the *intensity* of the single jar would be the greatest, for here the electricity would be less diffused. Faraday first satisfied himself that the needle of his galvanometer was caused to swing through the same arc by the same quantity of machine electricity, whether it was condensed in a small battery or diffused over a large one. Thus the electricity developed by thirty turns of his machine produced, under very variable conditions of battery surface, the same deflection. Hence he inferred the possibility of comparing, as regards quantity, electricities which differ greatly from each other in intensity.

His object now is to compare frictional with voltaic electricity. Moistening bibulous paper with the iodide of potassium—a favourite test of his—and subjecting it to the action of machine electricity, he decomposed the iodide, and formed a brown spot where the iodine is liberated. Then he immersed two wires, one of zinc, the other of platinum, each $\frac{1}{16}$ th of an inch in diameter, to a depth of $\frac{1}{16}$ ths of an inch in acidulated water during eight beats of his watch, or $\frac{1}{16}$ ths of a second; and found that the needle of his galvanometer swung through the same arc, and coloured his moistened paper to the same extent, as thirty turns of his large electrical machine. Twenty-eight turns of the machine produced an effect distinctly less than that produced by his two wires. Now, the quantity of water decomposed by the wires in this experiment totally eluded observation; it was immeasurably small; and still that amount of decomposition involved the development of a quantity of electric force which, if applied in a proper form, would kill a rat, and no man would like to bear it.

In his subsequent researches "on the absolute quantity of electricity associated with the particles or atoms of matter," he endeavours to give an idea of the amount of electrical force involved in the decomposition of a single grain of water. He is almost afraid to mention it, for he estimates it at 800,000 discharges of his large

Leyden battery. This, if concentrated in a single discharge, would be equal to a very great flash of lightning; while the chemical action of a single grain of water on four grains of zinc would yield electricity equal in quantity to a powerful thunderstorm. Thus his mind rises from the minute to the vast, expanding involuntarily from the smallest laboratory fact till it embraces the largest and grandest natural phenomena.*

In reality, however, he is at this time only clearing his way, and he continues laboriously to clear it for some time afterwards. He is digging the shaft, guided by that instinct towards the mineral lode which was to him a rod of divination. "*Er riecht die Wahrheit*," said the lamented Kohlrausch, an eminent German, once in my hearing:—"He smells the truth." His eyes are now steadily fixed on this wonderful voltaic current, and he must learn more of its mode of transmission.

On the 23rd of May, 1833, he read a paper before the Royal Society "On a new Law of Electric Conduction." He found that though the current passed through water, it did not pass through ice:—why not, since they are one and the same substance? Some years subsequently he answered this question by saying that the liquid condition enables the molecule of water to turn round so as to place itself in the proper line of polarization, while the rigidity of the solid condition prevents this arrangement. This polar arrangement must precede decomposition, and decomposition is an accompaniment of conduction. He then passed on to other substances; to oxides and chlorides, and iodides and salts, and sulphurets, and found them all insulators when solid, and conductors when fused. In all cases, moreover, except one—and this exception he thought might be apparent only—he found the passage of the current across the fused compound to be accompanied by its decomposition. Is then the act of decomposition essential to the act of conduction in these bodies? Even recently this question was warmly contested. Faraday was very cautious latterly in expressing himself upon this subject; but as a matter of fact he held that an infinitesimal quantity of electricity might pass through a compound liquid without producing its decomposition. De la Rive, who has been a great worker on the chemical phenomena of the pile, is very emphatic on the other side. Experiment, according to him and others, establishes in the most conclusive manner that no trace of electricity can pass through a liquid compound without producing its equivalent decomposition.†

* Buff finds the quantity of electricity associated with one milligramme of hydrogen in water, to be equal to 45,480 charges of a Leyden jar, with a height of 480 millimetres, and a diameter of 160 millimetres. Weber and Kohlrausch have calculated that if the quantity of electricity associated with one milligramme of hydrogen in water, were diffused over a cloud at a height of 1000 metres above the earth, it would exert upon an equal quantity of the opposite electricity at the earth's surface an attractive force of 2,268,000 kilogrammes.—*Electrolytische Maassbestimmungen*, 1866, p. 262.

† 'Faraday, sa Vie et ses Travaux,' p. 20.

Faraday has now got fairly entangled amid the chemical phenomena of the pile, and here his previous training under Davy must have been of the most important service to him. Why, he asks, should decomposition thus take place? what force is it that wrenches the locked constituent of these compounds asunder? On the 20th of June, 1833, he read a paper before the Royal Society "On Electro-Chemical Decomposition," in which he seeks to answer these questions. The notion had been entertained that the poles, as they are called, of the decomposing cell, or in other words the surfaces by which the current enters and quits the liquid, exercised electric attractions upon the constituents of the liquid and tore them asunder. Faraday combats this notion with extreme vigour. Litmus reveals, as you know, the action of an acid by turning red, turmeric reveals the action of an alkali by turning brown. Sulphate of soda, you know, is a salt compounded of the alkali soda and sulphuric acid. The voltaic current passing through a solution of this salt so decomposes it, that sulphuric acid appears at one pole of the decomposing cell and alkali at the other. Faraday steeped a piece of litmus paper and a piece of turmeric paper in a solution of sulphate of soda: placing each of them upon a separate plate of glass, he connected them together by means of a string moistened with the same solution. He then attached one of them to the positive conductor of an electric machine, and the other to the gas-pipes of this building. These he called his "discharging train." On turning the machine the electricity passed from paper to paper through the string, which might be varied in length from a few inches to seventy feet without changing the result. The first paper was reddened, declaring the presence of sulphuric acid; the second was browned, declaring the presence of the alkali soda. The dissolved salt, therefore, arranged in this fashion, was decomposed by the machine exactly as it would have been by the voltaic current. When instead of using the positive conductor he used the negative; the positions of the acid and alkali were reversed. Thus he satisfied himself that chemical decomposition by the machine is obedient to the laws which rule decomposition by the pile.

And now he gradually abolishes those so-called poles to the attraction of which electric decomposition had been ascribed. He connected a piece of turmeric paper moistened with the sulphate of soda with the positive conductor of his machine; then he placed a metallic point in connection with his discharging train opposite the moist paper, so that the electricity shall discharge through the air towards the point. The turning of the machine caused the corners of the piece of turmeric paper opposite to the point to turn brown, thus declaring the presence of alkali. He changed the turmeric for litmus paper, and placed it, not in connection with his conductor, but with his discharging train, a metallic point connected with the conductor being fixed at a couple of inches from the paper; on turning the machine, acid was liberated at the edges and corners of the litmus. He then placed a series of pointed pieces of paper, each separate piece being composed of two

halves, one of litmus and the other of turmeric paper, and all moistened with sulphate of soda, in the line of the current from the machine. The pieces of paper were separated from each other by spaces of air. The machine was turned; and it was always found that at the point where the electricity entered the paper, litmus was reddened, and at the point where it quitted the paper, turmeric was browned. "Here," he urges, "the poles are entirely abandoned, but we have still electro-chemical decomposition." It is evident to him that instead of being *attracted* by the poles, the bodies separated are *ejected* by the current. The effects thus obtained with poles of air he also succeeded in obtaining with poles of water. The advance in Faraday's own ideas made at this time is indicated by the word "ejected." He afterwards reiterates this view: the evolved substances are *expelled* from the decomposing body and "*not drawn out by an attraction.*"

Having abolished this idea of polar attraction, he proceeds to enunciate and develop a theory of his own. He refers to Davy's celebrated Bakerian Lecture given in 1806, which he says "is almost entirely occupied in the consideration of electro-chemical decompositions." The facts recorded in that lecture Faraday regards as of the utmost value. But "the mode of action by which the effects take place is stated very generally; so generally indeed, that probably a dozen precise schemes of electro-chemical action might be drawn up, differing essentially from each other, yet all agreeing with the statement there given."

It appears to me that these words might with justice be applied to Faraday's own researches at this time. They furnish us with results of permanent value; but little help can be found in the theory advanced to account for them. It would, perhaps, be more correct to say that the theory itself is hardly presentable in any tangible form to the intellect. Faraday looks, and rightly looks, into the heart of the decomposing body itself: he sees, and rightly sees, active within it the forces which produce the decomposition, and he rejects, and rightly rejects, the notion of external attraction; but beyond the hypothesis of decompositions and recompositions, enunciated and developed by Grothuss and Davy, he does not, I think, help us to any definite conception as to how the force reaches the decomposing mass and acts within it. Nor, indeed, can this be done, until we know the true physical process which underlies what we call an electric current.

Faraday conceives of that current as "*an axis of power having contrary forces exactly equal in amount in opposite directions;*" but this definition, though much quoted and circulated, teaches us nothing regarding the current. An "axis" here can only mean a direction; and what we want to be able to conceive of is, not the axis along which the power acts, but the nature and mode of action of the power itself. He objects to the vagueness of De la Rive; but the fact is that both he and De la Rive labour under the same difficulty. Neither wishes to commit himself to the notion of a current compounded of two electricities flowing in two opposite directions; but the time had not

come, nor is it yet come, for the displacement of this provisional fiction by the true mechanical conception. Still, however indistinct the theoretic notions of Faraday at this time may be, the facts which are rising before him and around him are leading him gradually, but surely, to results of incalculable importance in relation to the philosophy of the voltaic pile.

He had always some great object of research in view, but in the pursuit of it he frequently alighted on facts of collateral interest, to examine which he sometimes turned aside from his direct course. Thus we find the series of his researches on electro-chemical decomposition interrupted by an inquiry into "the power of metals and other solids, to induce the combination of gaseous bodies." This inquiry, which was received by the Royal Society on the 30th of November, 1833, though not so important as those which precede and follow it, illustrates throughout his strength as an experimenter. The power of spongy platinum to cause the combination of oxygen and hydrogen had been discovered by Doberciner in 1823, and had been applied by him in the construction of his well-known philosophic lamp. It was shown subsequently by Dulong and Thenard that even a platinum wire, when perfectly cleansed, may be raised to incandescence by its action on a jet of cold hydrogen.

In his experiments on the decomposition of water, Faraday found that the positive platinum plate of the decomposing cell possessed in an extraordinary degree the power of causing oxygen and hydrogen to combine. He traced the cause of this to the perfect cleanness of the positive plate. Against it was liberated oxygen, which with the powerful affinity of the "nascent state," swept away all impurity from the surface against which it was liberated. The bubbles of gas liberated on one of the platinum plates or wires of a decomposing cell are always much smaller, and they rise in much more rapid succession than those from the other. Knowing that oxygen is sixteen times heavier than hydrogen, I have more than once concluded, and, I fear, led others into the error of concluding, that the smaller and more quickly rising bubbles must belong to the lighter gas. The thing appeared so obvious that I did not give myself the trouble of looking at the battery, which would at once have told me the nature of the gas. But Faraday would never have been satisfied with a deduction if he could have reduced it to a fact. And he has taught me that the fact here is the direct reverse of what I supposed it to be. The small bubbles are oxygen, and their smallness is due to the perfect cleanness of the surface on which they are liberated. The hydrogen adhering to the other electrode swells into large bubbles, which rise in much slower succession; but when the current is reversed the hydrogen is liberated upon the cleansed wire, and then its bubbles also become small.

Laws of Electro-Chemical Decomposition.

In our conceptions and reasonings regarding the forces of nature, we perpetually make use of symbols which, when they possess a high representative value we dignify with the name of theories. Thus prompted by certain analogies we ascribe electrical phenomena to the action of a peculiar fluid, sometimes flowing, sometimes at rest. Such conceptions have their advantages and their disadvantages; they afford peaceful lodging to the intellect for a time, but they also circumscribe it, and by and by, when the mind has grown too large for its lodging, it often finds difficulty in breaking down the walls of what has become its prison instead of its home.*

No man ever felt this tyranny of symbols more deeply than Faraday, and no man was ever more assiduous than he to liberate himself from them and the terms which suggested them. Calling Dr. Whewell to his aid in 1833, he endeavoured to displace by others all terms tainted by a foregone conclusion. His paper on Electro-chemical decomposition, received by the Royal Society on the 9th of January, 1834, opens with the proposal of a new terminology. He would avoid the word "current" if he could † He does abandon the word "poles" as applied to the ends of a decomposing cell, because it suggests the idea of attraction, substituting for it the perfectly neutral term *electrodes*. He applied the term *electrolyte* to every substance which can be decomposed by the current, and the act of decomposition he calls *electrolysis*. All these terms have become current in science. He called the positive electrode the *Anode*, and the negative one the *Cathode*, but these terms, though frequently used, have not enjoyed the same currency as the others. The terms *Anion* and *Cation*, which he applied to the constituents of the decomposed electrolyte, and the term *ion*, which included both anions and cations, are still less frequently employed.

Faraday now passes from terminology to research; he sees the necessity of quantitative determinations, and seeks to supply himself with a measure of voltaic electricity. This he finds in the quantity of water decomposed by the current. He tests this measure in all possible ways, to assure himself that no error can arise from its employment. He places in the course of one and the same current a series of cells with electrodes of different sizes, some of them plates of platinum, others merely platinum wires, and collects the gas liberated on each distinct pair of electrodes. He finds the quantity of

* I copy these words from the printed abstract of a Friday evening lecture, given by myself, because they remind me of Faraday's voice, responding to the utterance by an emphatic *hear! hear!*—*Proceedings of the Royal Institution*, vol. ii., p. 132.

† In 1838 he expresses himself thus :—"The word current is so expressive in common language that when applied in the consideration of electrical phenomena, we can hardly divest it sufficiently of its meaning, or prevent our minds from being prejudiced by it."—*Exp. Researches*, vol. i., p. 515. (§ 1617.)

gas to be the same for all. Thus he concludes that when the same quantity of electricity is caused to pass through a series of cells containing acidulated water, the electro-chemical action is independent of the size of the electrodes. He next proves that variations in intensity do not interfere with this equality of action. Whether his battery is charged with strong acid or with weak; whether it consists of five pairs or of fifty pairs; in short, whatever be its source, when the same current is sent through his series of cells, the same amount of decomposition takes place in all. He next assures himself that the strength or weakness of his dilute acid does not interfere with this law. Sending the same current through a series of cells containing mixtures of sulphuric acid and water of different strengths, he finds, however the proportion of acid to water might vary, the same amount of gas to be collected in all the cells. A crowd of facts of this character forced upon Faraday's mind the conclusion that the amount of electro-chemical decomposition depends, not upon the size of the electrodes, not upon the intensity of the current, not upon the strength of the solution, but solely upon the quantity of electricity which passes through the cell. The quantity of electricity he concludes is proportional to the amount of chemical action. On this law Faraday based the construction of his celebrated voltameter, or measurer of voltaic electricity.

But before he can apply this measure he must clear his ground of numerous possible sources of error. The decomposition of his acidulated water is certainly a *direct* result of the current; but as the varied and important researches of MM. Becquerel, De la Rive, and others had shown, there are also *secondary* actions, which may materially interfere with and complicate the pure action of the current. These actions may occur in two ways: either the liberated *ion* may seize upon the electrode against which it is set free, forming a chemical compound with that electrode; or it may seize upon the substance of the electrolyte itself, and thus introduce into the circuit chemical actions over and above those due to the current. Faraday subjected these secondary actions to an exhaustive examination. Instructed by his experiments, and rendered competent by them to distinguish between primary and secondary results, he proceeds to establish the doctrine of "definite electro-chemical decomposition."

Into the same circuit he introduced his voltameter, which consisted of a graduated tube filled with acidulated water and provided with platinum plates for the decomposition of the water, and also a cell containing chloride of tin. Experiments already referred to had taught him that this substance, though an insulator when solid, is a conductor when fused, the passage of the current being always accompanied by the decomposition of the chloride. He wished now to ascertain what relation this decomposition bore to that of the water in his voltameter.

Completing his circuit, he permitted the current to continue until "a reasonable quantity of gas" was collected in the voltameter. The circuit was then broken, and the quantity of tin liberated compared

with the quantity of gas. The weight of the former was 3·2 grains, that of the latter 0·49742 of a grain. Oxygen, as you know, unites with hydrogen in the proportion of 8 to 1 to form water. Calling the equivalent, or, as it is sometimes called, the atomic weight of hydrogen 1, that of oxygen is 8; that of water is consequently $8 + 1$, or 9. Now if the quantity of water decomposed in Faraday's experiment be represented by the number 9, or in other words by the equivalent of water, then the quantity of tin liberated from the fused chloride is found by an easy calculation to be 57·9, which is almost exactly the chemical equivalent of tin. Thus both the water and the chloride were broken up in proportions expressed by their respective equivalents. The amount of electric force which wrenched asunder the constituents of the molecule of water was competent, and neither more nor less than competent, to wrench asunder the constituents of the molecules of the chloride of tin. The fact is typical. With the indications of his voltmeter he compared the decomposition of other substances both singly and in series. He submitted his conclusions to numberless tests. He purposely introduced secondary actions. He endeavoured to hamper the fulfilment of those laws which it was the intense desire of his mind to see established. But from all these difficulties emerged the golden truth, that under every variety of circumstances the decompositions of the voltaic current are as definite in their character as those chemical combinations which gave birth to the atomic theory. This law of electro-chemical decomposition ranks, in point of importance, with that of definite combining proportions in chemistry.

Origin of Power in the Voltaic Pile.

In one of the public areas of the town of Como stands a statue, with no inscription on its pedestal save that of a single name, "Volta." The bearer of that name occupies a place for ever memorable in the history of science. To him we owe the discovery of the voltaic pile, to which, for a brief interval, we must now turn our attention.

The objects of scientific thought being the passionless laws and phenomena of external nature, one might suppose that their investigation and discussion would be completely withdrawn from the region of the feelings, and pursued by the cold dry light of the intellect alone. This, however, is not always the case. Man carries his heart with him into all his works. You cannot separate the moral and emotional from the intellectual; and thus it is that the discussion of a point of science may rise to the heat of a battle-field. The fight between the rival optical theories of Emission and Undulation was of this fierce character; and scarcely less fierce for many years was the contest as to the origin and maintenance of the power of the voltaic pile. Volta himself supposed it to reside in the contact of different metals. Here was exerted his "electro-motive force," which tore the combined elec-

tricitities asunder and drove them as currents in opposite directions. To render the circulation of the current possible, it was necessary to connect the metals by a moist conductor; for when any two metals were connected by a third, their relation to each other was such that a complete neutralization of the electric motion was the result. Volta's theory of metallic contact was so clear, so beautiful, and apparently so complete, that the best intellects of Europe accepted it as the expression of natural law.

Volta himself knew nothing of the chemical phenomena of the pile; but as soon as these became known, suggestions and intimations appeared that chemical action, and not metallic contact, might be the real source of voltaic electricity. This idea was expressed by Fabroni in Italy and by Wollaston in England. It was developed and maintained by those "admirable electricians," Becquerel, of Paris, and De la Rive, of Geneva. The contact theory, on the other hand, received its chief development and illustration in Germany. It was long the scientific creed of the great chemists and natural philosophers of that country, and to the present hour there may be some of them unable to liberate themselves from the fascination of their first-love.

After the researches which I have endeavoured to place before you, it was impossible for Faraday to avoid taking a side in this controversy. He did so in a paper "On the Electricity of the Voltaic Pile," received by the Royal Society, on the 7th of April, 1834. His position in the controversy might have been predicted. He saw chemical effects going hand-in-hand with electrical effects, the one being proportional to the other; and, in the paper now before us, he proved that when the former were excluded, the latter were sought for in vain. He produced a current without metallic contact; he discovered liquids which, though competent to transmit the feeblest currents—competent therefore to allow the electricity of contact to flow through them if it were able to form a current—were absolutely powerless when chemically inactive.

One of the very few experimental mistakes of Faraday occurred in this investigation. He thought that with a single voltaic cell he had obtained the spark *before the metals touched*, but he subsequently discovered his error. To enable the voltaic spark to pass through air before the terminals of the battery were united, it was necessary to exalt the electro-motive force of the battery by multiplying its elements; but all the elements Faraday possessed were unequal to the task of urging the spark across the shortest measurable space of air. Nor, indeed, could the action of the battery, the different metals of which were in contact with each other, decide the point in question. Still as regards the identity of electricities from various sources, it was at that day of great importance to determine whether or not the voltaic current could jump as a spark across an interval before contact. Faraday's friend, Mr. Gassiot, solved this problem. He erected a battery of 4000 cells, and with it urged a stream of sparks from terminal to terminal, when separated from each other by a measurable space of air.

The memoir on the "Electricity of the Voltaic Pile," published in 1834, appears to have produced but little impression upon the supporters of the contact theory. These indeed were men of too great intellectual weight and insight lightly to take up, or lightly to abandon a theory. Faraday therefore resumed the attack in a paper communicated to the Royal Society, on the 6th of February, 1840. In this paper he hampered his antagonists by a crowd of adverse experiments. He hung difficulty after difficulty about the neck of the contact theory, until in its efforts to escape from his assaults it so changed its character as to become a thing totally different from the theory proposed by Volta. The more persistently it was defended, however, the more clearly did it show itself to be a congeries of devices, bearing the stamp of dialectic skill rather than that of natural truth.

In conclusion, Faraday brought to bear upon it an argument which, had its full weight and purport been understood at the time, would have instantly decided the controversy. "The contact theory," he urged, "assumes that a force which is able to overcome powerful resistance, as for instance that of the conductors, good or bad, through which the current passes, and that again of the electrolytic action where bodies are decomposed by it, *can arise out of nothing*: that without any change in the acting matter, or the consumption of any generating force, a current shall be produced which shall go on for ever against a constant resistance, or only be stopped, as in the voltaic trough, by the ruins which its exertion has heaped up in its own course. This would indeed be a *creation of power*, and is like no other force in nature. We have many processes by which the *form* of the power may be so changed, that an apparent *conversion* of one into the other takes place. So we can change chemical force into the electric current, or the current into chemical force. The beautiful experiments of Seebeck and Peltier show the convertibility of heat and electricity; and others by Oersted and myself show the convertibility of electricity and magnetism. *But in no case, not even in those of the Gymnotus and Torpedo, is there a pure creation or a production of power without a corresponding exhaustion of something to supply it.*"

These words were published more than two years before either Mayer printed his brief but celebrated essay on the Forces of Inorganic Nature, or Mr. Joule published his first famous experiments on the Mechanical Value of Heat. They illustrate the fact that before any great scientific principle receives distinct enunciation by individuals, it dwells more or less clearly in the general scientific mind. The intellectual plateau is already high, and our discoverers are those who, like peaks above the plateau, rise a little above the general level of thought at the time.

But many years prior, even to the foregoing utterance of Faraday, a similar argument had been employed. I quote here with equal pleasure and admiration the following passage written by Dr. Roget so far back as 1829. Speaking of the contact theory, he says:—"If there could exist a power having the property ascribed it to by the

hypothesis, namely, that of giving continual impulse to a fluid in one constant direction, without being exhausted by its own action, it would differ essentially from all the known powers in nature. All the powers and sources of motion with the operation of which we are acquainted, when producing these peculiar effects, are expended in the same proportion as those effects are produced; and hence arises the impossibility of obtaining by their agency a perpetual effect; or in other words a perpetual motion. But the electro-motive force, ascribed by Volta to the metals, when in contact, is a force which, as long as a free course is allowed to the electricity it sets in motion, is never expended, and continues to be excited with undiminished power in the production of a never-ceasing effect. Against the truth of such a supposition the probabilities are all but infinite." When this argument, which he employed independently, had clearly fixed itself in his mind, Faraday never cared to experiment further on the source of electricity in the voltaic pile. The argument appeared to him "to remove the foundation itself of the contact theory," and he afterwards let it crumble down in peace.*

Researches on Frictional Electricity: Induction: Conduction: Specific Inductive Capacity: Theory of Contiguous Particles.

The burst of power which had filled the four preceding years with an amount of experimental work unparalleled in the history of science partially subsided in 1835, and the only scientific paper contributed by Faraday in that year was a comparatively unimportant one, "On an improved Form of the Voltaic Battery." He brooded for a time: his experiments on electrolysis had long filled his mind; he looked, as already stated, into the very heart of the electrolyte, endeavouring to render the play of its atoms visible to his mental eye. He had no doubt that in this case what is called "the electric current" was propagated from particle to particle of the electrolyte; he accepted the doctrine of decomposition and recombination which, according to Grothuss and Davy, ran from electrode to electrode. And the thought impressed him more and more that ordinary electric induction was also transmitted and sustained by the action of "*contiguous particles*."

* To account for the *electric current*, which was really the core of the whole discussion, Faraday demonstrated the impotence of the contact theory as then enunciated and defended. Still, it is certain that two different metals, when brought into contact, charge themselves, the one with positive and the other with negative electricity. I had the pleasure of going over this ground with Kohlrausch in 1849, and his experiments left no doubt upon my mind that the contact electricity of Volta was a reality, though it could produce no current. With one of the beautiful instruments devised by himself, Sir William Thomson has rendered this point capable of sure and easy demonstration; and he and others now hold what may be called a contact theory, which, while it takes into account the action of the metals, also embraces the chemical phenomena of the circuit. Helmholtz, I believe, was the first to give the contact theory this new form, in his celebrated essay, *Ueber die Erhaltung der Kraft*, p. 45.

His first great paper on frictional electricity was sent to the Royal Society on the 30th of November, 1837. We here find him face to face with an idea which beset his mind throughout his whole subsequent life,—the idea of *action at a distance*. It perplexed and bewildered him. In his attempts to get rid of this perplexity he was often unconsciously rebelling against the limitations of the intellect itself. He loved to quote Newton upon this point: over and over again he introduces his memorable words, "That gravity should be innate, inherent, and essential to matter, so that one body may act upon another at a distance through a *vacuum* and without the mediation of anything else, by and through which this action and force may be conveyed from one to another, is to me so great an absurdity, that I believe no man who has in philosophical matters a competent faculty of thinking can ever fall into it. Gravity must be caused by an agent acting constantly according to certain laws; but whether this agent be material or immaterial I have left to the consideration of my readers."*

Faraday does not see the same difficulty in his contiguous particles. And yet by transferring the conception from masses to particles we simply lessen size and distance, but we do not alter the quality of the conception. Whatever difficulty the mind experiences in conceiving of action at sensible distances, besets it also when it attempts to conceive of action at insensible distances. Still the investigation of the point whether electric and magnetic effects were wrought out through the intervention of contiguous particles or not, had a physical interest altogether apart from the metaphysical difficulty. Faraday grapples with the subject experimentally. By simple intuition he sees that action at a distance must be exerted in straight lines. Gravity, he knows, will not turn a corner, but exerts its pull along a right line; hence his aim and effort to ascertain whether electric action ever takes place in curved lines. This once proved, it would follow that the action is carried on *by means of a medium* surrounding the electrified bodies. His experiments in 1837, reduced, in his opinion, this point to demonstration. He then found that he could electrify by induction an insulated sphere placed completely in the shadow of a body which screened it from direct action. He pictured the lines of electric force bending round the edges of the screen, and reuniting on the other side of it; and he proved that in many cases the augmentation of the distance between his insulated sphere and the inducing body, instead of lessening, increased the charge of the sphere. This he ascribed to the coalescence of the lines of electric force at some distance behind the screen.

Faraday's theoretic views on this subject have not received general acceptance, but they drove him to experiment, and experiment with him was always prolific of results. By suitable arrangements he places a metallic sphere in the middle of a large hollow sphere,

* Newton's third letter to Bentley.

leaving a space of something more than half-an-inch between them. The interior sphere was insulated, the external one uninsulated. To the former he communicated a definite charge of electricity. It acted by induction upon the concave surface of the latter, and he examined how this act of induction was effected by placing insulators of various kinds between the two spheres. He tried gases, liquids, and solids, but the solids alone gave him positive results. He constructed two instruments of the foregoing description, equal in size and similar in form. The interior sphere of each communicated with the external air by a brass stem ending in a knob. The apparatus was virtually a Leyden jar, the two coatings of which were the two spheres, with a thick and variable insulator between them. The amount of charge in each jar was determined by bringing a proof-plane into contact with its knob, and measuring by a torsion balance the charge taken away. He first charged one of his instruments, and then dividing the charge with the other, found that when air intervened in both cases, the charge was equally divided. But when shell-lac, sulphur, or spermaceti was interposed between the two spheres of one jar, while air occupied this interval in the other, then he found that the instrument occupied by the "solid dielectric" takes *more than half* the original charge. A portion of the charge was absorbed in the dielectric itself. The electricity took time to penetrate the dielectric. Immediately after the discharge of the apparatus no trace of electricity was found upon its knob. But after a time electricity was found there, the charge having gradually returned from the dielectric in which it had been lodged. Different insulators possess this power of permitting the charge to enter them in different degrees. Faraday figured their particles as polarized, and he concluded that the force of induction is propagated from particle to particle of the dielectric from the inner sphere to the outer one. This power of propagation possessed by insulators he calls their "*Specific Inductive Capacity*."

Faraday visualizes with the utmost clearness the state of his contiguous particles; one after another they become charged, each succeeding particle depending for its charge upon its predecessor. And now he seeks to break down the wall of partition between conductors and insulators. "Can we not," he says, "by a gradual chain of association carry up discharge from its occurrence in air through spermaceti and water to solutions, and then on to chlorides, oxides, and metals, without any essential change in its character?" Even copper, he urges, offers a resistance to the transmission of electricity. The action of its particles differs from those of an insulator only in degree. They are charged like the particles of the insulator, but they discharge with greater ease and rapidity; and this rapidity of molecular discharge is what we call conduction. Conduction then is always preceded by atomic induction; and when through some quality of the body, which Faraday does not define, the atomic discharge is rendered slow and difficult, conduction passes into insulation.

Though they are often obscure, a fine vein of philosophic thought

runs through those investigations. The mind of the philosopher dwells amid those agencies which underlie the visible phenomena of Induction and Conduction; and he tries by the strong light of his imagination to see the very molecules of his dielectrics. It would, however, be easy to criticize these researches, easy to show the looseness, and sometimes the inaccuracy, of the phrasology employed; but this critical spirit will get little good out of Faraday. Rather let those who ponder his works seek to realize the object he set before him, not permitting his occasional vagueness to interfere with their appreciation of his speculations. We may see the ripples, and eddies, and vortices of a flowing stream, without being able to resolve all these motions into their constituent elements; and so it sometimes strikes me that Faraday clearly saw the play of fluids and ethers and atoms, though his previous training did not enable him to resolve what he saw into its constituents, or describe it in a manner satisfactory to a mind versed in mechanics. And then again occur, I confess, dark sayings, difficult to be understood, which disturb my confidence in this conclusion. It must, however, always be remembered that he works at the very boundaries of our knowledge, and that his mind habitually dwells in the "boundless contiguity of shade" by which that knowledge is surrounded.

In the researches now under review the ratio of speculation and reasoning to experiment is far higher than in any of Faraday's previous works. Amid much that is entangled and dark we have flashes of wondrous insight and utterances which seem less the product of reasoning than of revelation. I will confine myself here to one example of this divining power:—By his most ingenious device of a rapidly rotating mirror, Wheatstone had proved that electricity required time to pass through a wire, the current reaching the middle of the wire later than its two ends. "If," says Faraday, "the two ends of the wire in Professor Wheatstone's experiments were immediately connected with two large insulated metallic surfaces exposed to the air, so that the primary act of induction, after making the contact for discharge, might be in part removed from the internal portion of the wire at the first instance, and disposed for the moment on its surface jointly with the air and surrounding conductors, then I venture to anticipate that the middle spark would be more retarded than before. And if those two plates were the inner and outer coatings of a large jar or Leyden battery, then the retardation of the spark would be much greater." This was only a *prediction*, for the experiment was not made.* Sixteen years subsequently, however, the proper conditions came into play, and Faraday was able to show that the observations of Werner Siemens, and Latimer Clark, on subterraneous and submarine wires were illustrations, on a grand

* If Sir Charles Wheatstone could be induced to take up his measurements once more, varying the substances through which, and the conditions under which the current is propagated, he might render great service to science, both theoretic and experimental.

scale, of the principle which he had enunciated in 1838. The wires and the surrounding water act as a Leyden jar, and the retardation of the current predicted by Faraday manifests itself in every message sent by such cables.

The meaning of Faraday in these memoirs on Induction and Conduction is, as I have said, by no means always clear; and the difficulty will be most felt by those who are best trained in ordinary theoretic conceptions. He does not know the reader's needs, and he therefore does not meet them. For instance, he speaks over and over again of the impossibility of charging a body with one electricity, though the impossibility is by no means evident. The key to the difficulty is this. He looks upon every insulated conductor as the inner coating of a Leyden jar. An insulated sphere in the middle of a room is to his mind such a coating; the walls are the outer coating, while the air between both is the insulator, across which the charge acts by induction. Without this reaction of the walls upon the sphere you could no more, according to Faraday, charge it with electricity than you could charge a Leyden jar, if its outer coating were removed. Distance with him is immaterial. His strength as a generalizer enables him to dissolve the idea of magnitude; and if you abolished the walls of the room—even the earth itself—he would make the sun and planets the outer coating of his jar. I dare not contend that Faraday in these memoirs made all his theoretic positions good. But a pure vein of philosophy runs through these writings; while his experiments and reasonings on the forms and phenomena of electrical discharge are of imperishable importance.

Rest needed—Visit to Switzerland.

The last of these memoirs was dated from the Royal Institution in June, 1838. It concludes the first volume of his 'Experimental Researches on Electricity.' In 1840, as already stated, he made his final assault on the contact theory, from which it never recovered.* He was now feeling the effects of the mental strain to which he had been subjected for so many years. During these years he repeatedly broke down. His wife alone witnessed the extent of his prostration, and to her loving care we, and the world, are indebted for the enjoyment of his presence here so long. He found occasional relief in a theatre. He frequently quitted London and went to Brighton and elsewhere, always choosing a situation which commanded a view of the sea, or of some other pleasant horizon, where he could sit and gaze and feel the gradual revival of the faith that

"Nature never did betray
The heart that loved her."

But very often for some days after his removal to the country he would be unable to do more than sit at a window and look out upon the sea and sky.

* See note, p. 77

In 1841, his state became more serious than it had ever been before. A published letter to Mr. Richard Taylor, dated March 11, 1843, contains an allusion to his previous condition. "You are aware," he says, "that considerations regarding health have prevented me from working or reading on science for the last two years." This, at one period or another of their lives, seems to be the fate of most great investigators. They do not know the limits of their constitutional strength until they have transgressed them. It is, perhaps, right that they should transgress them, in order to ascertain where they lie. Faraday, however, though he went far towards it, did not push his transgression beyond his power of restitution. In 1841 Mrs. Faraday and he went to Switzerland, under the affectionate charge of her brother, Mr. George Barnard, the artist. This time of suffering throws fresh light upon his character. I have said that sweetness and gentleness were not its only constituents; that he was also fiery and strong. At the time now referred to his fire was low and his strength distilled away; but the residue of his life was neither irritability nor discontent. He was unfit to mingle in society, for conversation was a pain to him; but let us observe the great Man-child when alone. He is at the village of Interlaken, enjoying Jungfrau sunsets, and at times watching the Swiss nailers making their nails. He keeps a little journal, in which he describes the process of nail-making, and incidentally throws a luminous beam upon himself.

"August 2nd, 1841. Clout nail-making goes on here rather considerably, and is a very neat and pretty operation to observe. I love a smith's shop and anything relating to smithery. *My father was a smith.*"

From Interlaken he went to the Falls of the Giessbach, on the pleasant lake of Brienz. And here we have him watching the shoot of the cataract down its series of precipices. It is shattered into foam at the base of each, and tossed by its own recoil as water-dust through the air. The sun is at his back, shining on the drifting spray, and he thus describes and muscs on what he sees :—

"August 12th, 1841. To-day every fall was foaming from the abundance of water, and the current of wind brought down by it was in some places too strong to stand against. The sun shone brightly, and the rainbows seen from various points were very beautiful. One at the bottom of a fine but furious fall was very pleasant,—there it remained motionless whilst the gusts and clouds of spray swept furiously across its place and were dashed against the rock. It looked like a spirit strong in faith and steadfast in the midst of the storm of passions sweeping across it, and though it might fade and revive, still it held on to the rock as in hope and giving hope. And the very drops, which in the whirlwind of their fury seemed as if they would carry all away, were made to revive it and give it greater beauty."

Magnetization of Light.

But we must quit the man and go on to the discoverer : we shall return for a brief space to his company by and by. Carry your thoughts back to his last experiments, and see him endeavouring to prove that induction is due to the action of contiguous particles. He knew that polarized light was a most subtle and delicate investigator of molecular condition. He used it in 1834 in exploring his electrolytes, and he tried it in 1838 upon his dielectrics. At that time he coated two opposite faces of a glass cube with tinfoil, connected one coating with his powerful electric machine and the other with the earth, and examined by polarized light the condition of the glass when thus subjected to strong electric influence. He failed to obtain any effect, still he was persuaded an action existed, and required only suitable means to call it forth.

After his return from Switzerland he was beset by these thoughts : they were more inspired than logical ; but he resorted to magnets and proved his inspiration true. His dislike of "doubtful knowledge" and his efforts to liberate his mind from the thralldom of hypotheses have been already referred to. Still this rebel against theory was incessantly theorizing himself. His principal researches are all connected by an undercurrent of speculation. Theoretic ideas were the very sap of his intellect—the source from which all his strength as an experimenter was derived. While once sauntering with him through the Crystal Palace, at Sydenham, I asked him what directed his attention to the magnetization of light. It was his theoretic notions. He had certain views regarding the unity and convertibility of natural forces ; certain ideas regarding the vibrations of light and their relations to the lines of magnetic force ; these views and ideas drove him to investigation. And so it must always be : the great experimentalist must ever be the habitual theorist, whether or not he gives to his theories formal enunciation.

Faraday, you must have been informed, endeavoured to improve the manufacture of glass for optical purposes. But though he produced a heavy glass of great refractive power, its value to optics did not repay him for the pains and labour bestowed on it. Now, however, we reach a result established by means of this same heavy glass, which made ample amends for all.

In November, 1845, he announced his discovery of the "Magnetization of Light, and the Illumination of the Lines of Magnetic Force." This title provoked comment at the time, and caused misapprehension. He therefore added an explanatory note ; but the note left his meaning as entangled as before. In fact, Faraday had notions regarding the magnetization of light which were peculiar to himself, and untranslatable into the scientific language of the time. Probably no other philosopher of his day would have employed the phrases just quoted as appropriate to the discovery announced in 1845. But Faraday was more than a philosopher ; he was a prophet, and often wrought

by an inspiration to be understood by sympathy alone. The prophetic element in his character occasionally coloured and even injured the utterance of the man of science; but subtracting that element, though you might have conferred on him intellectual symmetry, you would have destroyed his motive force.

But let us pass from the label of this casket to the jewel it contains. "I have long," he says, "held an opinion almost amounting to conviction, in common I believe with many other lovers of natural knowledge, that the various forms under which the forces of matter are made manifest have one common origin; in other words, are so directly related and mutually dependent, that they are convertible, as it were, into one another, and possess equivalents of power in their action. . . . This strong persuasion," he adds, "extended to the powers of light." And then he examines the action of magnets upon light. From conversation with him and Anderson, I should infer that the labour preceding this discovery was very great. The world knows little of the toil of the discoverer. It sees the climber jubilant on the mountain-top, but does not know the labour expended in reaching it. Probably hundreds of experiments had been made on transparent crystals before he thought of testing his heavy glass. Here is his own clear and simple description of the result of his first experiment with this substance:—"A piece of this glass, about two inches square, and 0.5 of an inch thick, having flat and polished edges, was placed as a *diamagnetic** between the poles (not as yet magnetized by the electric current), so that the polarized ray should pass through its length; the glass acted as air, water, or any other transparent substance would do; and if the eye-piece were previously turned into such a position that the polarized ray was extinguished, or rather the image produced by it rendered invisible, then the introduction of the glass made no alteration in this respect. In this state of circumstances, the force of the electro-magnet was developed by sending an electric current through its coils, and immediately the image of the lamp-flame became visible, and continued so long as the arrangement continued magnetic. On stopping the electric current, and so causing the magnetic force to cease, the light instantly disappeared. These phenomena could be renewed at pleasure, at any instant of time, and upon any occasion, showing a perfect dependence of cause and effect."

In a beam of ordinary light the particles of the luminiferous ether vibrate in all directions perpendicular to the line of progression; by the act of polarization, performed here by Faraday, all oscillations but those parallel to a certain plane are eliminated. When the plane of vibration of the polarizer coincides with that of the analyzer, a portion

* "By a *diamagnetic*," says Faraday, "I mean a body through which lines of magnetic force are passing, and which does not by their action assume the usual magnetic state of iron or loadstone." Faraday subsequently used this term in a different sense from that here given, as will immediately appear.

of the beam passes through both; but when these two planes are at right angles to each other, the beam is extinguished. If by any means, while the polarizer and analyzer remain thus crossed, the plane of vibration of the polarized beam between them could be changed, then the light would be, in part at least, transmitted. In Faraday's experiment this was accomplished. His magnet turned the plane of polarization of the beam through a certain angle, and thus enabled it to get through the analyzer; so that "the magnetization of light and the illumination of the magnetic lines of force" becomes when expressed in the language of modern theory, *the rotation of the plane of polarization*.

To him, as to all true philosophers, the main value of a fact was its position and suggestiveness in the general sequence of scientific truth. Hence, having established the existence of a phenomenon, his habit was to look at it from all possible points of view, and to develop its relationship to other phenomena. He proved that the direction of the rotation depends upon the polarity of his magnet; being reversed when the magnetic poles are reversed. He showed that when a polarized ray passed through his heavy glass in a direction parallel to the magnetic lines of force, the rotation is a maximum, and that when the direction of the ray is at right angles to the lines of force there is no rotation at all. He also proved that the amount of the rotation is proportional to the length of the diamagnetic through which the ray passes. He operated with liquids and solutions. Of aqueous solutions he tried 150 and more, and found the power in all of them. He then examined gases; but here all his efforts to produce any sensible action upon the polarized beam were ineffectual. He then passed from magnets to currents, enclosing bars of heavy glass, and tubes containing liquids and aqueous solutions within an electro-magnetic helix. A current sent through the helix caused the plane of polarization to rotate, and always in the *direction of the current*. The rotation was reversed when the current was reversed. In the case of magnets, he observed a gradual, though quick, ascent of the transmitted beam from a state of darkness to its maximum brilliancy when the magnet was excited. In the case of currents, the beam attained *at once* its maximum. This he showed to be due to the *time* required by the iron of the electro-magnet to assume its full magnetic power, which time vanishes when a current without iron is employed. "In this experiment," he says, "we may, I think, justly say that a ray of light is electrified, and the electric forces illuminated." In the helix, as with the magnets, he submitted *air* to magnetic influence "carefully and anxiously," but could not discover any trace of action on the polarized ray.

Many substances possess the power of turning the plane of polarization without the intervention of magnetism. Oil of turpentine and quartz are examples: but Faraday showed that, while in one direction, that is, across the lines of magnetic force, his rotation is zero, augmenting gradually from this until it attains its maximum, when the direction of the ray is parallel to the lines of force, in the oil of

turpentine, the rotation is independent of the direction of the ray. But he showed that a still more profound distinction exists between the magnetic rotation and the natural one. I will try to explain how. Suppose a tube with glass ends containing oil of turpentine to be placed north and south. Fixing the eye at the south end of the tube, let a polarized beam be sent through it from the north. To the observer in this position the rotation of the plane of polarization, by the turpentine, is *right-handed*. Let the eye be placed at the north end of the tube and a beam be sent through it from the south: the rotation is still right-handed. Not so, however, when a bar of heavy glass is subjected to the action of an electric current. In this case if, in the first position of the eye, the rotation be right-handed, in the second position it is left-handed. These considerations make it manifest that if a polarized beam, after having passed through the oil of turpentine in its natural state, could, by any means, be reflected back through the liquid, the rotation impressed upon the direct beam would be exactly neutralized by that impressed upon the reflected one. Not so with the induced magnetic effect. Here it is manifest that the rotation would be doubled by the act of reflection. Hence Faraday concludes that the particles of the oil of turpentine which rotate by virtue of their natural force, and those which rotate in virtue of the induced force, cannot be in the same condition. The same remark applies to all bodies which possess a natural power of rotating the plane of polarization.

And then he proceeded with exquisite skill and insight to take advantage of this conclusion. He silvered the ends of his piece of heavy glass, leaving, however, a narrow portion parallel to two edges diagonally opposed to each other unsilvered. He then sent his beam through this uncovered portion, and by suitably inclining his glass caused the beam within it to reach his eye, first direct, and then after two, four, and six reflections. These corresponded to the passage of the ray once, three times, five times, and seven times through the glass. He thus established with numerical accuracy the exact proportionality of the rotation to the distance traversed by the polarized beam. Thus in one series of experiments where the rotation acquired by the direct beam was 12° , that acquired by three passages through the glass was 36° , while that acquired by five passages was 60° . But even when this method of magnifying was applied, he failed with various solid substances to obtain any effect; and in the case of air, though he employed to the utmost the power which these repeated reflections placed in his hands, he failed to produce the slightest sensible rotation.

These failures of Faraday to obtain the effect with gases, seem to indicate the true seat of the phenomenon. The luminiferous ether surrounds and is influenced by the ultimate particles of matter. The symmetry of the one involves that of the other. Thus, if the molecules of a crystal be perfectly symmetrical round any line through the crystal, we may safely conclude that a ray will pass along this line

as through ordinary glass. It will not be doubly refracted. From the symmetry of the liquid figures, known to be produced in the planes of freezing, when radiant heat is sent through ice, we may safely infer symmetry of aggregation, and hence conclude that the line perpendicular to the planes of freezing is a line of no double refraction : that it is, in fact, the optic axis of the crystal. The same remark applies to the line joining the opposite blunt angles of a crystal of Iceland spar. The arrangement of the molecules round this line being symmetrical, the condition of the ether depending upon these molecules shares their symmetry ; and there is, therefore, no reason why the wave-length should alter with the alteration of the azimuth round this line. Annealed glass has its molecules symmetrically arranged round every line that can be drawn through it ; hence it is not doubly refractive. But let the substance be either squeezed or strained in one direction, the molecular symmetry, and with it the symmetry of the ether, is immediately destroyed and the glass becomes doubly refractive. Unequal heating produces the same effect. Thus mechanical strains reveal themselves by optical effects ; and there is little doubt that in Faraday's experiment it is the *magnetic strain* that produces the rotation of the plane of polarization.*

Discovery of Diamagnetism—Researches on Magneto-Crystalline Action.

Faraday's next great step in discovery was announced in a memoir on the "Magnetic Condition of all Matter," communicated to the Royal Society on the 18th of December, 1845. One great source of his success was the employment of extraordinary power. As already stated, he never accepted a negative answer to an experiment until he had brought to bear upon it all the force at his command. He had over and over again tried steel magnets and ordinary electro-magnets on various substances, but without detecting anything different from the ordinary attraction exhibited by a few of them. Stronger coercion, however, developed a new action. Before the pole of an electro-magnet, he suspended a fragment of his famous heavy glass ; and observed that when the magnet was powerfully excited the glass fairly retreated from the pole. It was a clear case of magnetic *repulsion*. He then suspended a bar of the glass between two poles ; the bar retreated when the poles were excited, and set its length *equatorially*

* The power of double refraction conferred on the centre of a glass rod, when it is caused to sound the fundamental note due to its longitudinal vibration, and the absence of the same power in the case of vibrating air (enclosed in a glass organ-pipe), seems to be analogous to the presence and absence of Faraday's effect in the same two substances.

Faraday never, to my knowledge, attempted to give, even in conversation, a picture of the molecular condition of his heavy glass when subjected to magnetic influence. In a mathematical investigation of the subject, published in the Proceedings of the Royal Society for 1856, Sir William Thomson arrives at the conclusion that the "diamagnetic" is in a state of molecular *rotation*.

or at right angles to the line joining them. When an ordinary magnetic body was similarly suspended, it always set *axially*, that is, from pole to pole.

Faraday called those bodies which were repelled by the poles of a magnet, *diamagnetic* bodies; using this term in a sense different from that in which he employed it in his memoir on the magnetization of light. The term *magnetic* he reserved for bodies which exhibited the ordinary attraction. He afterwards employed the term magnetic to cover the whole phenomena of attraction and repulsion, and used the word *paramagnetic* to designate such magnetic action as is exhibited by iron.

Isolated observations by Brugnaams, Becquerel, le Baillif, Saigy, and Seebeck had indicated the existence of a repulsive force exercised by the magnet on two or three substances; but these observations, which were unknown to Faraday, had been permitted to remain without extension or examination. Having laid hold of the fact of repulsion, Faraday immediately expanded and multiplied it. He subjected bodies of the most various qualities to the action of his magnet: - mineral salts, acids, alkalis, ethers, alcohols, aqueous solutions, glass, phosphorus, various oils, essences, vegetable and animal tissues, and found them all amenable to magnetic influence. No known solid or liquid proved insensible to the magnetic power when developed in sufficient strength. All the tissues of the human body, the blood - though it contains iron - included, were proved to be diamagnetic. So that if you could suspend a man between the poles of a magnet, his extremities would retreat from the poles until his length became equatorial.

Soon after he had commenced his researches on diamagnetism, Faraday noticed a remarkable phenomenon which first crossed my own path in the following way: In the year 1849, while working in the cabinet of my friend, Professor Knoblauch, of Marburg, I suspended a small copper coin between the poles of an electro-magnet. On exciting the magnet, the coin moved towards the poles and then suddenly stopped, as if it had struck against a cushion. On breaking the circuit, the coin was repelled, the revulsion being so violent as to cause it to spin several times round its axis of suspension. A *Silbergroschen* similarly suspended exhibited the same deportment. For a moment I thought this a new discovery; but on looking over the literature of the subject, it appeared that Faraday had observed, multiplied, and explained the same effect during his researches on diamagnetism. His explanation was based upon his own great discovery of magneto-electric currents. The effect is a most singular one. A weight of several pounds of copper may be set spinning between the electro-magnetic poles; the excitement of the magnet instantly stops the rotation. Though nothing is apparent to the eye, the copper, if moved in the excited magnetic field, appears to move through a viscous fluid; while, when a flat piece of the metal is caused to pass to and fro like a saw between the poles, the sawing of the magnetic field

resembles the cutting through of cheese or butter.* This virtual *friction* of the magnetic field is so strong that copper by its rapid rotation between the poles might probably be fused. We may easily dismiss this experiment by saying that the heat is due to the electric currents excited in the copper. But so long as we are unable to reply to the question, "What is an electric current?" the explanation is only provisional. For my own part, I look with profound interest and hope on the strange action here referred to.

Faraday's thoughts ran intuitively into experimental combinations, so that subjects whose capacity for experimental treatment would to ordinary minds seem to be exhausted in a moment, were shown by him to be all but inexhaustible. He has now an object in view, the first step towards which is the proof that the principle of Archimedes is true of magnetism. He forms magnetic solutions of various degrees of strength, places them between the poles of his magnet, and suspends in the solutions various magnetic bodies. He proves that when the solution is stronger than the body plunged in it, the body, though magnetic, is repelled; and when an elongated piece of it is surrounded by the solution it sets, like a diamagnetic body, equatorially between the excited poles. The same body when suspended in a solution of weaker magnetic power than itself is attracted as whole, while an elongated portion of it sets axially.

And now theoretic questions rush in upon him. Is this new force a true repulsion, or is it merely a differential attraction? Might not the apparent repulsion of diamagnetic bodies be really due to the greater attraction of the medium by which they are surrounded? He tries the rarefaction of air, but finds the effect insensible. He is averse to ascribing a capacity of attraction to space, or to any hypothetical medium supposed to fill space. He therefore inclines, but still with caution, to the opinion that the action of a magnet upon bismuth is a true and absolute repulsion, and not merely the result of differential attraction. And then he clearly states a theoretic view sufficient to account for the phenomena. "Theoretically," he says, "an explanation of the movements of the diamagnetic bodies, and all the dynamic phenomena consequent upon the action of magnets upon them, might be offered in the supposition that magnetic induction caused in them a contrary state to that which it produced in ordinary matter." That is to say, while in ordinary magnetic influence the exciting pole excites adjacent to itself the contrary magnetism, in diamagnetic bodies the adjacent magnetism is the same as that of the exciting pole. This theory of reversed polarity, however, does not appear to have ever laid deep hold of Faraday's mind; and his own experiments failed to give any evidence of its truth. He therefore subsequently abandoned it, and maintained the *non-polarity* of the diamagnetic force.

He then entered a new, though related field of inquiry. Having

* See 'Heat as a Mode of Motion,' 3rd edition, § 36.

dealt with the metals and their compounds, and having classified all of them that came within the range of his observation under the two heads magnetic and diamagnetic, he began the investigation of the phenomena presented by crystals when subjected to magnetic power. The action of crystals had been in part theoretically predicted by Poisson,* and actually discovered by Plucker, whose beautiful results, at the period which we have now reached, profoundly interested all scientific men. Faraday had been frequently puzzled by the deportment of bismuth, a highly crystalline metal. Sometimes elongated masses of the substance refused to set equatorially, sometimes they set persistently oblique, and sometimes even, like a magnetic body, from pole to pole. "The effect," he says, "occurs at a single pole; and it is then striking to observe a long piece of a substance so diamagnetic as bismuth repelled, and yet at the same moment set round with force, axially, or end on, as a piece of magnetic substance would do." The effect perplexed him; and in his efforts to release himself from this perplexity, no feature of this new manifestation of force escaped his attention. His experiments are described in a memoir communicated to the Royal Society on the 7th of December, 1848.

I have "long myself at magne-crystalline action, amid all the light of Faraday's and Plucker's researches. The papers now before me were objects of daily and nightly study with me eighteen or nineteen years ago; but even now, though their perusal is but the last of a series of repetitions, they astonish me. Every circumstance connected with the subject; every shade of deportment; every variation in the energy of the action; almost every application which could possibly be made of magnetism to bring out in detail the character of this new force, is minutely described. The field is swept clean and hardly anything experimental is left for the gleaner. The phenomena he concludes are altogether different from those of magnetism or diamagnetism; they would appear in fact to present to us "a new force, or a new form of force, in the molecules of matter," which for convenience sake he designates by a new word, as "*the magne-crystalline force*."

He looks at the crystal acted upon by the magnet. From its mass he passes, in idea, to its atoms, and he asks himself whether the power which can thus seize upon the crystalline molecules, after they have been fixed in their proper positions by crystallizing force, may not, when they are free, be able to determine their arrangement? He therefore liberates the atoms by fusing the bismuth. He places the fused substance between the poles of an electro-magnet, powerfully excited; but he fails to detect any action. I think it cannot be doubted that an action is exerted here, that a true cause comes into play; but its magnitude is not such as sensibly to interfere with the force of crystallization, which, in comparison with the diamagnetic force, is enormous. "Perhaps," adds Faraday, "if a longer time

* See Sir William Thomson on Magne-crystalline Action, 'Phil. Mag.,' 1851.

were allowed and a permanent magnet used, a better result might be obtained. I had built many hopes upon the process." This expression, and his writings abound in such, illustrates what has been already said regarding his experiments being suggested and guided by his theoretic conceptions. His mind was full of hopes and hypotheses, but he always brought them to an experimental test. The record of his planned and executed experiments would, I doubt not, show a high ratio of hopes disappointed to hopes fulfilled: but every case of fulfilment abolished all memory of defeat; disappointment was swallowed up in victory.

After the description of the general character of this new force, Faraday states with the emphasis here reproduced its mode of action: "The law of action appears to be that *the line or axis of MAGNE-CRYSTALLIC force* (being the resultant of the action of all the molecules) *tends to place itself parallel, or as a tangent, to the magnetic curve, or line of magnetic force, passing through the place where the crystal is situated.*" The magne-crystalline force, moreover, appears to him "to be clearly distinguished from the magnetic or diamagnetic forces, in that it causes neither approach nor recession, consisting not in attraction or repulsion, but in giving a certain determinate position to the mass under its influence." And then he goes on "very carefully to examine and prove the conclusion that there was no connection of the force with attractive or repulsive influences." With the most refined ingenuity he shows that, under certain circumstances, the magne-crystalline force can cause the centre of gravity of a highly magnetic body to retreat from the poles, and the centre of gravity of a highly diamagnetic body to approach them. His experiments root his mind more and more firmly in the conclusion that it is "neither attraction nor repulsion causes the set, or governs the final position" of the crystal in the magnetic field. That the force which does so is therefore "distinct in its character and effects from the magnetic and diamagnetic forms of force. On the other hand," he continues, "it has a most manifest relation to the crystalline structure of bismuth and other bodies, and therefore to the power by which their molecules are able to build up the crystalline masses."

And here follows one of those expressions which characterize the conceptions of Faraday in regard to force generally: "It appears to me impossible to conceive of the results in any other way than by a mutual reaction of the magnetic force, and the force of the particles of the crystal upon each other." He proves that the action of the force though thus molecular is an action at a distance; he shows that a bismuth crystal can cause a freely suspended magnetic needle to set parallel to its magne-crystalline axis. Few living men are aware of the difficulty of obtaining results like this, or of the delicacy necessary to their attainment. "But though it thus takes up the character of a force acting at a distance, still it is due to that power of the particles which makes them cohere in regular order and gives the mass its crystalline aggregation, which we call at other times the attraction

of aggregation, and so often speak of as acting at *insensible* distances." Thus he broods over this new force, and looks at it from all possible points of inspection. Experiment follows experiment, as thought follows thought. He will not relinquish the subject as long as a hope exists of throwing more light upon it. He knows full well the anomalous nature of the conclusion to which his experiments lead him. But experiment to him is final, and he will not shrink from the conclusion. "This force," he says, "appears to me to be very strange and striking in its character. It is not polar, for there is no attraction or repulsion." And then, as if startled by his own utterance, he adds: - "What is the nature of the mechanical force which turns the crystal round, and makes it attract a magnet?" . . . "I do not remember," he continues, "heretofore such a case of force as the present one, where a body is brought into position only, without attraction or repulsion."

Plucker, the celebrated geometer already mentioned, who pursued experimental physics for many years of his life with singular devotion and success, visited Faraday in those days, and repeated before him his beautiful experiments on magneto optic action. Faraday repeated and verified Plucker's observations, and concluded, what he at first seemed to doubt, that Plucker's results and magneto-crystalline action have the same origin.

At the end of his papers, when he takes a last look along the line of research, and then turns his eyes to the future, utterances quite as much emotional as scientific escape from Faraday. "I cannot," he says, at the end of his first paper on magneto-crystalline action, "conclude this series of researches without remarking how rapidly the knowledge of molecular forces grows upon us, and how strikingly every investigation tends to develop more and more their importance, and their extreme attraction as an object of study. A few years ago magnetism was to us an occult power, affecting only a few bodies, now it is found to influence all bodies, and to possess the most intimate relations with electricity, heat, chemical action, light, crystallization, and through it, with the forces concerned in cohesion; and we may, in the present state of things, well feel urged to continue in our labours, encouraged by the hope of bringing it into a bond of union with gravity itself."

Supplementary Remarks.

A brief space will, perhaps, be granted me here to state the further progress of an investigation which interested Faraday so much. Drawn by the fame of Bunsen as a teacher, in the year 1818 I became a student in the University of Marburg, in Hesse-Cassel. Bunsen behaved to me as a brother as well as a teacher, and it was also my happiness to make the acquaintance and gain the friendship of Professor Knoblauch, so highly distinguished by his researches on Radiant Heat. Plucker's and Faraday's investigations filled all minds at the time, and towards the end of 1819, Professor Knoblauch and

myself commenced a joint investigation of the entire question. Long discipline was necessary to give us due mastery over it. Employing a method proposed by Dove, we examined the optical properties of our crystals ourselves; and these optical observations went hand in hand with our magnetic experiments. The number of these experiments was very great, but for a considerable time no fact of importance was added to those already published. At length, however, it was our fortune to meet with various crystals whose deportment could not be brought under the laws of magne-crystalline action enunciated by Plücker. We also discovered instances which led us to suppose that the magne-crystalline force was by no means independent, as alleged, of the magnetism or diamagnetism of the mass of the crystal. Indeed, the more we worked at the subject, the more clearly did it appear to us that the deportment of crystals in the magnetic field was due, not to a force previously unknown, but to the modification of the known forces of magnetism and diamagnetism by crystalline aggregation.

An eminent example of magne-crystalline action adduced by Plücker and experimented on by Faraday, was Iceland spar. It is what in optics is called a *negative* crystal, and according to the law of Plücker, the axis of such a crystal was always repelled by a magnet. But we showed that it was only necessary to substitute, in whole or in part, carbonate of iron for carbonate of lime, thus changing the magnetic but not the optical character of the crystal, to cause the axis to be attracted. That the deportment of magnetic crystals is exactly antithetical to that of diamagnetic crystals isomorphous with the magnetic ones, was proved to be a general law of action. In all cases, the line which in a diamagnetic crystal set equatorially, always set itself in an isomorphous magnetic crystal axially. By mechanical compression other bodies were also made to imitate the Iceland spar.

These and numerous other results bearing upon the question were published at the time in the 'Philosophical Magazine' and in 'Poggendorff's Annalen;' and the investigation of diamagnetism and magne-crystalline action was subsequently continued by me in the laboratory of Professor Magnus of Berlin. In December, 1851, after I had quitted Germany, Dr. Bence Jones went to the Prussian capital to see the celebrated experiments of Du Bois Reymond; and influenced, I suppose, by what he heard, he afterwards invited me to give a Friday evening discourse at the Royal Institution. I consented, not without fear and trembling. For the Royal Institution was to me a kind of dragon's den, where tact and strength would be necessary to save me from destruction. On February 11, 1853, the discourse was given, and it ended happily. I allude to these things that I may mention that though my aim and object in that lecture was to subvert the notions both of Faraday and Plücker, and to establish in opposition to their views what I regarded as the truth, it was very far from producing in Faraday either enmity or anger. At the conclusion of the lecture, he quitted his accustomed seat, crossed the theatre to the corner into which I had shrunk, shook me by the hand,

and brought me back to the table. Once more, subsequently, and in connection with a related question, I ventured to differ from him still more emphatically. It was done out of trust in the greatness of his character; nor was the trust misplaced. He felt my public dissent from him; and it pained me afterwards to the quick to think that I had given him even momentary annoyance. It was, however, only momentary. His soul was above all littleness and proof to all egotism. He was the same to me afterwards that he had been before; the very chance expression which led me to conclude that he felt my dissent being one of kindness and affection.

It required long subsequent effort to subdue the complications of magne-crystalline action, and to bring under the dominion of elementary principles the vast mass of facts which the experiments of Faraday and Plucker had brought to light. It was proved by Reich, Edmond Becquerel, and myself, that the condition of diamagnetic bodies in virtue of which they were repelled by the poles of a magnet, was excited in them by those poles; that the strength of this condition rose and fell with, and was proportional to, the strength of the acting magnet. It was not then any property possessed permanently by the bismuth, and which merely required the development of magnetism to act upon it, that caused the repulsion, for then the repulsion would have been simply proportional to the strength of the influencing magnet, whereas experiment proved it to augment as the square of the strength. The capacity to be repelled was therefore not inherent in the bismuth, but *induced*. So far an identity of action was established between magnetic and diamagnetic bodies. After this the deportment of magnetic bodies, "normal" and "abnormal," crystalline, amorphous, and compressed, was compared with that of crystalline, amorphous, and compressed diamagnetic bodies; and by a series of experiments, executed in the laboratory of this Institution, the most complete antithesis was established between magnetism and diamagnetism. This antithesis embraced the quality of polarity,—the theory of reversed polarity, first propounded by Faraday, being proved to be true. The discussion of the question was very brisk. On the continent Professor Wilhelm Weber was the ablest and most successful supporter of the doctrine of diamagnetic polarity; and it was with an apparatus, devised by him and constructed under his own superintendence, by Leyser of Leipzig, that the last demands of the opponents of diamagnetic polarity were satisfied. The establishment of this point was absolutely necessary to the explanation of magne-crystalline action.

With that admirable instinct which always guided him, Faraday had seen that it was possible, if not probable, that the diamagnetic force acts with different degrees of intensity in different directions, through the mass of a crystal. In his studies on electricity he had sought an experimental reply to the question whether crystalline bodies had not different specific inductive capacities in different directions, but he failed to establish any difference of the kind. His first attempt to

establish differences of diamagnetic action in different directions through bismuth, was also a failure: but he must have felt this to be a point of cardinal importance, for he returned to the subject in 1850, and proved that bismuth was repelled with different degrees of force in different directions. It seemed as if the crystal were compounded of two diamagnetic bodies of different strengths, the substance being more strongly repelled across the magne-crystalline axis than along it. The same result was obtained independently, and extended to various other bodies, magnetic as well as diamagnetic, and also to compressed substances, a little subsequently by myself. The law of action in relation to this point is, that in diamagnetic crystals, the line along which the repulsion is a maximum, sets equatorially in the magnetic field; while in magnetic crystals the line along which the attraction is a maximum sets from pole to pole. Faraday had said that the magne-crystalline force was neither attraction nor repulsion. Thus far he was right. It was neither, taken singly, *but it was both*. By the combination of the doctrine of diamagnetic polarity with these differential attractions and repulsions, and by paying due regard to the character of the magnetic field, every fact brought to light in the domain of magne-crystalline action received complete explanation. The most perplexing of those facts were shown to result from the action of mechanical couples, which the proved polarity both of magnetism and diamagnetism brought into play. Indeed the thoroughness with which the experiments of Faraday were thus explained, is the most striking possible demonstration of the marvellous precision with which they were executed.

Magnetism of Flame and Gases: Atmospheric Magnetism.

When an experimental result was obtained by Faraday it was instantly enlarged by his imagination. I am acquainted with no mind whose power and suddenness of expansion at the touch of new physical truth could be ranked with his. Sometimes I have compared the action of his experiments on his mind to that of highly combustible matter thrown into a furnace: every fresh entry of fact was accompanied by the immediate development of light and heat. The light, which was intellectual, enabled him to see far beyond the boundaries of the fact itself, and the heat, which was emotional, urged him to the conquest of this newly-revealed domain. But though the force of his imagination was enormous, he bridled it like a mighty rider, and never permitted his intellect to be overthrown.

In virtue of the expansive power which his vivid imagination conferred upon him, he rose from the smallest beginnings to the grandest ends. Having heard from Zantedeschi that Bancalari had established the magnetism of flame, he repeated the experiments and augmented the results. He passed from flames to gases, examining and revealing their magnetic and diamagnetic powers; and then he sud-

denly rose from his bubbles of oxygen and nitrogen to the atmospheric envelope of the earth itself, and its relations to the great question of terrestrial magnetism. The rapidity with which these ever-augmenting thoughts assumed the form of experiments is unparalleled. His power in this respect is often best illustrated by his minor investigations, and, perhaps, by none more strikingly than by his paper "On the Diamagnetic Condition of Flame and Gases," published as a letter to Mr. Richard Taylor, in 'The Philosophical Magazine' for December, 1847. After verifying, varying, and expanding the results of Bancalari, he submitted to examination heated air-currents, produced by platinum spirals, placed in the magnetic field, and raised to incandescence by electricity. He then examined the magnetic deportment of gases generally. Almost all of these gases are invisible; but he must, nevertheless, track them in their unseen courses. He could not effect this by mingling smoke with his gases, for the action of his magnet upon the smoke would have troubled his conclusions. He, therefore, "caught" his gases in tubes, carried them out of the magnetic field, and made them reveal themselves at a distance from the magnet.

Immersing one gas in another, he determined their differential action; results of the utmost beauty being thus arrived at. Perhaps the most important are those obtained with atmospheric air and its two constituents. *Oxygen*, in various media, was strongly attracted by the magnet; in coal-gas, for example, it was powerfully magnetic, whereas *nitrogen* was diamagnetic. Some of the effects obtained with oxygen in coal-gas were strikingly beautiful. When the fumes of chloride of ammonia (a diamagnetic substance) were mingled with the oxygen, the cloud of chloride behaved in a most singular manner: "The attraction of iron filings," says Faraday, "to a magnetic pole is not more striking than the appearance presented by the oxygen under these circumstances." On observing this deportment the question immediately occurs to him, - Can we not separate the oxygen of the atmosphere from its nitrogen by magnetic analysis? It is the perpetual occurrence of such questions that marks the great experimenter. The attempt to analyze atmospheric air by magnetic force proved a failure, like the previous attempt to influence crystallization by the magnet. The enormous comparative power of the force of crystallization was then assigned as a reason for the incompetence of the magnet to determine molecular arrangement: in the present instance the magnetic analysis is opposed by the force of diffusion, which is also very strong comparatively. The same remark applies to, and is illustrated by, another experiment subsequently executed by Faraday. Water is diamagnetic, sulphate of iron strongly magnetic. He enclosed "a dilute solution of sulphate of iron in a tube, and placed the lower end of the tube between the poles of a powerful horseshoe magnet for days together," but he could produce "no concentration of the solution in the part near the magnet." Here also the diffusibility of the salt was too powerful for the force brought against it.

The experiment last referred to is recorded in a paper presented to the Royal Society on the 2nd of August, 1850, in which he pursues the investigation of the magnetism of gases. Newton's observations on soap-bubbles were often referred to by Faraday. His delight in a soap-bubble was like that of a boy, and he often introduced them in his lectures, causing them, when filled with air, to float on invisible seas of carbonic acid, and otherwise employing them as means of illustration. He now finds them exceedingly useful in his experiments on the magnetic condition of gases. A bubble of air in a magnetic field occupied by air was unaffected, save through the feeble repulsion of its envelope. A bubble of nitrogen, on the contrary, was repelled from the magnetic axis with a force far surpassing that of a bubble of air. The deportment of oxygen in air "was very impressive, the bubble being pulled inward, or towards the axial line, sharply and suddenly, as if the oxygen were highly magnetic."

He next labours to establish the true magnetic zero, a problem not so easy as might at first sight be imagined. For the action of the magnet upon any gas, while surrounded by air, or any other gas, can only be differential; and if the experiment were made in vacuo, the action of the envelope, in this case necessarily of a certain thickness, would trouble the result. While dealing with this subject Faraday makes some note-worthy observations regarding *space*. In reference to the Torricellian vacuum, he says, "Perhaps it is hardly necessary for me to state that I find both iron and bismuth in such vacua, perfectly obedient to the magnet. From such experiments, and also from general observations and knowledge, it seems manifest that the lines of magnetic force can traverse pure space, just as gravitating force does, and as statical electrical forces do, and therefore space has a magnetic relation of its own, and one that we shall probably find hereafter to be of the utmost importance in natural phenomena. But this character of space is not of the same kind as that which, in relation to matter, we endeavour to express by the terms magnetic and diamagnetic. To confuse these together would be to confound space with matter, and to trouble all the conceptions by which we endeavour to understand and work out a progressively clearer view of the mode of action, and the laws of natural forces. It would be as if in gravitation or electric forces, one were to confound the particles acting on each other with the space across which they are acting, and would, I think, shut the door to advancement. Mere space cannot act as matter acts, even though the utmost latitude be allowed to the hypothesis of an ether; and admitting that hypothesis, it would be a large additional assumption to suppose that the lines of magnetic force are vibrations carried on by it, whilst as yet we have no proof that time is required for their propagation, or in what respect they may, in general character, assimilate to or differ from the respective lines of gravitating luminiferous or electric forces."

Pure space he assumes to be the true magnetic zero, but he pushes his inquiries to ascertain whether among material substances there

may not be some which resemble space. If you follow his experiments you will soon emerge into the light of his results. A torsion beam was suspended by a skein of cocoon silk; at one end of the beam was fixed a cross-piece $1\frac{1}{2}$ inches long. Tubes of exceedingly thin glass, filled with various gases, and hermetically sealed, were suspended in pairs from the two ends of the cross-piece. The position of the rotating torsion head was such that the two tubes were at opposite sides of, and equidistant from, the magnetic axis, that is to say from the line joining the two closely approximated polar points of an electro magnet. His object was to compare the magnetic action of the gases in the two tubes. When one tube was filled with oxygen, and the other with nitrogen, on the superintention of the magnetic force, the oxygen was pulled towards the axis, the nitrogen being pushed out. By turning the torsion head they could be restored to their primitive position of equidistance, where it is evident the action of the glass envelopes was annulled. The amount of torsion necessary to re-establish equidistance, expressed the *magnetic difference* of the substances compared.

And then he compared oxygen with oxygen at different pressures. One of his tubes contained the gas at the pressure of 30 inches of mercury, another at a pressure of 15 inches of mercury, a third at a pressure of 10 inches, while a fourth was exhausted as far as a good air-pump renders exhaustion possible. "When the first of these was compared with the other three, the effect was most striking." It was drawn towards the axis when the magnet was excited, the tube containing the rarer gas being apparently driven away, and the greater the difference between the densities of the two gases, the greater was the energy of this action.

And now observe his mode of reaching a *material* magnetic zero. When a bubble of nitrogen was exposed in air in the magnetic field, on the superintention of the power, the bubble retreated from the magnet. A less acute observer would have set nitrogen down as diamagnetic; but Faraday knew that retreat in a medium composed in part of oxygen might be due to the attraction of the latter gas, instead of to the repulsion of the gas immersed in it. But if nitrogen be really diamagnetic, then a bubble or bulb filled with the dense gas will overcome one filled with the rarer gas. From the cross-piece of his torsion-balance he suspended his bulbs of nitrogen, at equal distances from the magnetic axis, and found that the rarefaction, or the condensation of the gas in either of the bulbs had not the slightest influence. When the magnetic force was developed, the bulbs remained in their first position, even when one was *filled* with nitrogen, and the other as far as possible *exhausted*. Nitrogen, in fact, acted "like space itself;" it was neither magnetic nor diamagnetic.

He cannot conveniently compare the paramagnetic force of oxygen with iron, in consequence of the exceeding magnetic intensity of the latter substance; but he does compare it with the sulphate of iron, and finds that, bulk for bulk, oxygen is equally magnetic with

a solution of this substance in water "containing seventeen times the weight of the oxygen in crystallized proto-sulphate of iron, or 3·4 times its weight of metallic iron in that state of combination." By its capability to deflect a fine glass fibre, he finds that the attraction of his bulb of oxygen, containing only 0·117 of a grain of the gas, at an average distance of more than an inch from the magnetic axis, is about equal to the gravitating force of the same amount of oxygen as expressed by its weight.

These facts could not rest for an instant in the mind of Faraday without receiving that expansion, to which I have already referred. "It is hardly necessary," he writes, "for me to say here that this oxygen cannot exist in the atmosphere exerting such a remarkable and high amount of magnetic force, without having a most important influence on the disposition of the magnetism of the earth, as a planet; especially, if it be remembered that its magnetic condition is greatly altered by variations of its density and by variations of its temperature. I think I see here the real cause of many of the variations of that force, which have been, and are now so carefully watched on different parts of the surface of the globe. The daily variation, and the annual variation, both seem likely to come under it; also very many of the irregular continual variations, which the photographic process of record renders so beautifully manifest. If such expectations be confirmed, and the influence of the atmosphere be found able to produce results like these, then we shall probably find a new relation between the aurora borealis and the magnetism of the earth, namely, a relation established, more or less, through the air itself in connection with the space above it; and even magnetic relations and variations, which are not as yet suspected, may be suggested and rendered manifest and measurable, in the further development of what I will venture to call *Atmospheric Magnetism*. I may be over-sanguine in these expectations, but as yet I am sustained in them by the apparent reality, simplicity, and sufficiency of the cause assumed, as it at present appears to my mind. As soon as I have submitted these views to a close consideration, and the test of accordance with observation, and, where applicable, with experiments also, I will do myself the honour to bring them before the Royal Society."

Two elaborate memoirs are then devoted to the subject of Atmospheric Magnetism; the first sent to the Royal Society on the 9th of October, and the second on the 19th of November, 1850. In these memoirs he discusses the effects of heat and cold upon the magnetism of the air, and the action on the magnetic needle, which must result from thermal changes. By the convergence and divergence of the lines of terrestrial magnetic force, he shows how the distribution of magnetism, in the earth's atmosphere, is affected. He applies his results to the explanation of the annual and of the diurnal variation: he also considers irregular variations, including the action of magnetic storms. He discusses, at length, the observations at St. Petersburg, Greenwich, Hobarton, St. Helena, Toronto, and the Cape of Good

Hope; believing that the facts, revealed by his experiments, furnish the key to the variations observed at all these places.

In the year 1851 I had the honour of an interview with Humboldt in Berlin, and his parting words to me then were, "Tell Faraday that I entirely agree with him, and that he has, in my opinion, completely explained the variation of the declination." Eminent men have since informed me that Humboldt was hasty in expressing this opinion. In fact, Faraday's memoirs on atmospheric magnetism lost much of their force—perhaps too much—through the important discovery of the relation of the variation of the declination to the number of the solar spots. But I agree with him and M. Edmond Becquerel, who worked independently at this subject, in thinking that a body so magnetic as oxygen, swathing the earth, and subject to variations of temperature, diurnal and annual, must affect the manifestations of terrestrial magnetism.* The air that stands upon a single square foot of the earth's surface is, according to Faraday, the equivalent in magnetic force to 8160lbs. of crystallized proto-sulphate of iron. Such a substance cannot be absolutely neutral as regards the deportment of the magnetic needle. But Faraday's writings on this subject are so voluminous, and the theoretic points are so novel and intricate, that I shall postpone the complete analysis of these researches to a time when I can lay hold of them more completely than my other duties allow me to do now.

Speculations: Nature of Matter: Lines of Force.

The scientific picture of Faraday would not be complete without a reference to his speculative writings. On Friday, January 19, 1844, he opened the weekly evening meetings of the Royal Institution by a discourse entitled "A speculation touching Electric Conduction and the nature of Matter." In this discourse he not only attempts the overthrow of Dalton's Theory of Atoms, but also the subversion of all ordinary scientific ideas regarding the nature and relations of Matter and Force. He objected to the use of the term atom:—"I have not yet found a mind," he says, "that did habitually separate it from its accompanying temptations; and there can be no doubt that the words definite proportions, equivalent, primes, &c., which did and do fully express all the *facts* of what is usually called the atomic theory in chemistry, were dismissed because they were not expressive enough, and did not say all that was in the mind of him who used the word atom in their stead."

A moment will be granted me to indicate my own view of Faraday's position here. The word "atom" was not used in the stead of definite proportions, equivalents, or primes. These terms represented **facts**

* This persuasion has been greatly strengthened by the recent perusal of a paper by Mr. Baxendell.

that followed from, but were not equivalent to the atomic theory. Facts cannot satisfy the mind: and the law of definite combining proportions being once established, the question "why should combination take place according to that law?" is inevitable. Dalton answered this question by the enunciation of the Atomic Theory, the fundamental idea of which is, in my opinion, perfectly secure. The objection of Faraday to Dalton might be urged with the same substantial force against Newton: it might be stated with regard to the planetary motions that the laws of Kepler revealed the *facts*; that the introduction of the principle of gravitation was an addition to the facts. But this is the essence of *all* theory. The theory is the backward guess from fact to principle; the conjecture, or divination regarding something, which lies behind the facts, and from which they flow in necessary sequence. If Dalton's theory then account for the definite proportions observed in the combinations of chemistry, its justification rests upon the same basis as that of the principle of gravitation. All that can in strictness be said in either case is that the facts occur *as if* the principle existed.

The manner in which Faraday himself habitually deals with his hypotheses is revealed in this lecture. He incessantly employed them to gain experimental ends, but he incessantly took them down, as an architect removes the scaffolding when the edifice is complete. "I cannot but doubt," he says, "that he who as a mere philosopher has most power of penetrating the secrets of nature, and *guessing by hypothesis* at her mode of working, will also be most careful for his own safe progress, and that of others, to distinguish the knowledge which consists of assumption, by which I mean theory and hypothesis, from that which is the knowledge of facts and laws." Faraday himself, in fact, was always "guessing by hypothesis," and making theoretic divination the stepping-stone to his experimental results.

I have already more than once dwelt on the vividness with which he realized molecular conditions: we have a fine example of this strength and brightness of imagination in the present "speculation." He grapples with the notion that matter is made up of particles, not in absolute contact, but surrounded by interatomic space. "Space," he observes, "must be taken as the only *continuous part* of a body so constituted. Space will permeate all masses of matter in every direction like a net, except that in place of meshes it will form cells, isolating each atom from its neighbours, itself only being continuous."

Let us follow out this notion; consider, he argues, the case of a non-conductor of electricity, such for example as shell-lac, with its molecules, and their intermolecular spaces running through the mass. In its case space must be an insulator; for if it were a conductor it would resemble "*a fine metallic web*" penetrating the lac in every direction. But the fact is that it resembles the wax of black sealing-wax which surrounds and insulates the particles of conducting carbon, interspersed throughout its mass. In the case of shell-lac, therefore, *space is an insulator*.

But now take the case of a conducting metal. Here we have as before, the swathing of space round every atom. If space be an insulator there can be no transmission of electricity from atom to atom. But there *is* transmission; hence *space is a conductor*. Thus he endeavours to hamper the atomic theory. "The reasoning," he says, "ends in a subversion of that theory altogether; for if space be an insulator it cannot exist in conducting bodies, and if it be a conductor it cannot exist in insulating bodies. Any ground of reasoning," he adds, as if carried away by the ardour of argument, "which tends to such conclusions as these must in itself be false."

He then tosses the atomic theory from horn to horn of his dilemmas. What do we know, he asks, of the atom apart from its force? You imagine a nucleus which may be called a , and surround it by forces which may be called m ; "to my mind the a or nucleus vanishes, and the substance consists in the powers of m . And indeed what notion can we form of the nucleus independent of its powers? What thought remains on which to hang the imagination of an a independent of the acknowledged forces." Like Boscovich he abolishes the atom and puts a "centre of force" in its place.

With heroic courage and sincerity he pushes his view to its utmost consequences. "This view of the constitution of matter," he continues, "would seem to involve necessarily the conclusion that matter fills all space, or at least all space to which gravitation extends; for gravitation is a property of matter dependent on a certain force, and it is this force which constitutes the matter. In that view matter is not merely mutually penetrable;* but each atom extends, so to say, throughout the whole of the solar system, yet always retaining its own centre of force."

It is the operation of a mind filled with thoughts of this profound, strange, and subtle character that we have to take into account in dealing with Faraday's later researches. A similar cast of thought pervades a letter addressed by Faraday to Mr. Richard Phillips, and published in the 'Philosophical Magazine' for May, 1846. It is entitled 'Thoughts on Ray-vibrations,' and it contains one of the most singular speculations that ever emanated from a scientific mind. It must be remembered here, that though Faraday lived amid such speculations he did not rate them highly, and that he was prepared at any moment to change them or let them go. They spurred him on, but they did not hamper him. His theoretic notions were *fluent*; and when minds less plastic than his own attempted to render those fluxional images rigid, he rebelled. He warns Phillips, moreover, that from first to last "he merely threw out as matter for speculation the vague impressions of his mind; for he gave nothing as the result of sufficient consideration, or as the settled conviction, or even probable conclusion at which he had arrived."

* He compares the interpenetration of two atoms to the coalescence of two distinct waves, which though for a moment blended to a single mass, preserve their individuality, and afterwards separate.

The gist of this communication is that gravitating force acts in lines across space, and that the vibrations of light and radiant heat consist in the tremors of these lines of force. "This notion," he says, "as far as it is admitted, will dispense with the ether, which, in another view, is supposed to be the medium in which these vibrations take place." And he adds further on, that his view "endeavours to dismiss the ether but not the vibrations." The idea here set forth is the natural supplement of his previous notion that it is gravitating force which constitutes matter, each atom extending, so to say, throughout the whole of the solar system.

The letter to Mr. Phillips winds up with this beautiful conclusion :--

"I think it likely that I have made many mistakes in the preceding pages, for even to myself my ideas on this point appear only as the shadow of a speculation, or as one of those impressions upon the mind which are allowable for a time as guides to thought and research. He who labours in experimental inquiries, knows how numerous these are, and how often their apparent fitness and beauty vanish before the progress and development of real natural truth."

Let it then be remembered that Faraday entertained notions regarding matter and force altogether distinct from the views generally held by scientific men. Force seemed to him an entity dwelling along the line in which it is exerted. The lines along which gravity acts between the sun and earth seem figured in his mind as so many elastic strings: indeed he accepts the assumed instantaneity of gravity as the expression of the enormous elasticity of the "lines of weight." Such views, fruitful in the case of magnetism, barren as yet in the case of gravity, explain his efforts to transform this latter force. When he goes into the open air and permits his helices to fall, to his mind's eye they are tearing through the lines of gravitating power, and hence his hope and conviction that an effect would and ought to be produced. It must ever be borne in mind that Faraday's difficulty in dealing with these conceptions was at bottom the same as that of Newton; that he is in fact trying to overleap this difficulty, and with it probably the limits prescribed to the intellect itself.

The idea of lines of magnetic force was suggested to Faraday by the linear arrangement of iron filings when scattered over a magnet. He speaks of and illustrates by sketches, the deflection, both convergent and divergent, of the lines of force, when they pass respectively through magnetic and diamagnetic bodies. These notions of concentration and divergence are also based on the direct observation of his filings. So long did he brood upon these lines; so habitually did he associate them with his experiments on induced currents, that the association became "indissoluble," and he could not think without them. "I have been so accustomed," he writes, "to employ them, and especially in my last researches, that I may have unwittingly become prejudiced in their favour, and ceased to be a clear-sighted judge. Still, I have always endeavoured to make experiment the test

and controller of theory and opinion; but neither by that nor by close cross-examination in principle, have I been made aware of any error involved in their use."

In his later researches on magne-crystalline action, the idea of lines of force is extensively employed; it indeed led him to an experiment which lies at the root of the whole question. In his subsequent researches on Atmospheric Magnetism the idea receives still wider application, showing itself to be wonderfully flexible and convenient. Indeed without this conception the attempt to seize upon the magnetic actions, possible or actual, of the atmosphere would be difficult in the extreme; but the notion of lines of force, and of their divergence and convergence, guides Faraday without perplexity through all the intricacies of the question. After the completion of those researches, and in a paper forwarded to the Royal Society on the 22nd of October, 1851, he devotes himself to the formal development and illustration of his favourite idea. The paper bears the title "On lines of magnetic force, their definite character, and their distribution within a magnet and through space." A deep reflectiveness is the characteristic of this memoir. In his experiments, which are perfectly beautiful and profoundly suggestive, he takes but a secondary delight. His object is to illustrate the utility of his conception of lines of force. "The study of these lines," he says, "has at different times been greatly influential in leading me to various results which I think prove their utility as well as fertility."

Faraday for a long period used the lines of force merely as "a representative idea." He seemed for a time averse to going further in expression than the lines themselves, however much further he may have gone in idea. That he believed them to exist at all times round a magnet, and irrespective of the existence of magnetic matter, such as iron filings, external to the magnet, is certain. No doubt the space round every magnet presented itself to his imagination as traversed by loops of magnetic power, but he was chary in speaking of the physical substratum of those loops. Indeed it may be doubted whether the *physical theory* of lines of force presented itself with any distinctness to his own mind. The possible complicity of the luminiferous ether in magnetic phenomena was certainly in his thoughts. "How the magnetic force," he writes, "is transferred through bodies or through space we know not; whether the result is merely action at a distance, as in the case of gravity; or by some intermediate agency, as in the case of light, heat, the electric current, and (as I believe) static electric action. The idea of magnetic fluids, as applied by some, or of magnetic centres of action, does not include that of the latter kind of transmission, *but the idea of lines of force does.*" And he continues thus:—"I am more inclined to the notion that in the transmission of the [magnetic] force there is such an action [an intermediate agency] external to the magnet, than that the effects are merely attraction and repulsion at a distance. *Such an affection may be a function of the ether; for it is not at all unlikely that, if there be an*

ether, it should have other uses than simply the conveyance of radiations." When he speaks of the magnet in certain cases, "revolving amongst its own forces," he appears to have some conception of this kind in view.

A great part of the investigation completed in October, 1851, was taken up with the motions of wires round the poles of a magnet, and the converse. He carried an insulated wire along the axis of a bar magnet from its pole to its equator, where it issued from the magnet, and was bent up so as to connect its two ends. A complete circuit, no part of which was in contact with the magnet, was thus obtained. He found that when the magnet and the external wire were rotated together no current was produced; whereas, when *either* of them was rotated and the other left at rest currents were evolved. He then abandoned the axial wire, and allowed the magnet itself to take its place; the result was the same.* It was the *relative* motion of the magnet and the loop that was effectual in producing a current.

The lines of force have their roots in the magnet, and though they may expand into infinite space, they eventually return to the magnet. Now these lines may be intersected close to the magnet or at a distance from it. Faraday finds *distance* to be perfectly immaterial so long as the *number* of lines intersected is the same. For example, when the loop connecting the equator and the pole of his bar-magnet performs one complete revolution round the magnet, it is manifest that all the lines of force issuing from the magnet are *once* intersected. Now it matters not whether the loop be ten feet or ten inches in length, it matters not how it may be twisted and contorted, it matters not how near to the magnet or how distant from it the loop may be, one revolution always produces the same amount of current electricity, because in all these cases all the lines of force issuing from the magnet are *once* intersected and no more.

From the external portion of the circuit he passes in idea to the internal, and follows the lines of force into the body of the magnet itself. His conclusion is that there exists lines of force within the magnet of the same *nature* as those without. What is more, they are exactly equal in *amount* to those without. They have a relation in *direction* to those without; and in fact are continuations of them. . . . "Every line of force, therefore, at whatever distance it may be taken from the magnet, must be considered as a closed circuit, passing in some part of its course through the magnet, and having an equal amount of force in every part of its course."

All the results here described were obtained with *moving metals*. "But," he continues with profound sagacity, "mere motion would not generate a relation, which had not a foundation in the existence of some previous state; and therefore the *quiescent* metals must be in some relation to the active centre of force," that is to the magnet. He

* In this form the experiment is identical with one made twenty years earlier.

hero touches the core of the whole question, and when we can state the condition into which the conducting wire is thrown *before* it is moved, we shall then be in a position to understand the physical constitution of the electric current generated by its motion.

In this inquiry Faraday worked with steel magnets, the force of which varies with the distance from the magnet. He then sought a *uniform field* of magnetic force, and found it in space as affected by the magnetism of the earth. His next memoir, sent to the Royal Society on the 31st of December, 1851, is "On the employment of the Induced Magneto-electro Current as a test and measure of magnetic forces." He forms rectangles and rings, and by ingenious and simple devices collects the opposed currents which are developed in them by rotation across the terrestrial lines of magnetic force. He varies the shapes of his rectangles while preserving their areas constant, and finds that the constant area produces always the same amount of current per revolution. The current depends solely on the number of lines of force intersected, and when this number is kept constant the current remains constant too. Thus the lines of magnetic force are continually before his eyes, by their aid he colligates his facts, and through the inspirations derived from them he vastly expands the boundaries of our experimental knowledge. The beauty and exactitude of the results of this investigation are extraordinary. I cannot help thinking while I dwell upon them that this discovery of magneto-electricity is the greatest experimental result ever obtained by an investigator. It is the Mont Blanc of Faraday's own achievements. He always worked at great elevations, but a higher than this he never subsequently attained.

Unity and Convertibility of Natural Forces: Theory of the Electric Current.

The terms *unity* and *convertibility*, as applied to natural forces, are often employed in these investigations, many profound and beautiful thoughts respecting these subjects being expressed in Faraday's memoirs. Modern inquiry has however much augmented our knowledge of the relationship of natural forces, and it seems worth while to say a few words here, tending to clear up certain misconceptions which appear to exist among philosophic writers regarding this relationship.

The whole stock of *energy* or *working-power* in the world consists of *attractions*, *repulsions*, and *motions*. If the attractions and repulsions are so circumstanced as to be able to produce motion, they are sources of working-power, but not otherwise. Let us for the sake of simplicity confine our attention to the case of attraction. The attraction exerted between the earth and a body at a distance from the earth's surface is a source of working-power; because the body can be moved by the attraction, and in falling to the earth can perform work. When it rests upon the earth's surface it is *not* a source of power or energy,

because it can fall no further. But though it has ceased to be a source of *energy*, the attraction of gravity still acts as a *force*, which holds the earth and weight together.

The same remarks apply to attracting atoms and molecules. As long as distance separates them, they can move across it in obedience to the attraction, and the motion thus produced may, by proper appliances, be caused to perform mechanical work. When, for example, two atoms of hydrogen unite with one of oxygen, to form water, the atoms are first drawn towards each other they move, they clash, and then by virtue of their resiliency, they recoil and *quiver*. To this quivering motion we give the name of heat. Now this quivering motion is merely the redistribution of the motion produced by the chemical affinity; and this is the only sense in which chemical affinity can be said to be converted into heat. We must not imagine the chemical *attraction* destroyed, or converted into anything else. For the atoms when mutually clasped to form a molecule of water, are held together by the very attraction which first drew them towards each other. That which has really been expended is the *pull* exerted through the space by which the distance between the atoms has been diminished.

If this be understood it will be at once seen that *gravity* may in this sense be said to be convertible into heat; that it is in reality no more an outstanding and inconvertible agent, as it is sometimes stated to be, than chemical affinity. By the exertion of a certain pull through a certain space a body is caused to clash with a certain definite velocity against the earth. Heat is thereby developed, and this is the only sense in which gravity can be said to be converted into heat. In no case is the *force* which produces the motion annihilated or changed into anything else. The mutual *attraction* of the earth and weight exists when they are in contact as when they were separate; but the ability of that attraction to employ itself in the production of motion does *not* exist.

The transformation, in this case, is easily followed by the mind's eye. First, the weight as a whole is set in motion by the attraction of gravity. This motion of the mass is arrested by collision with the earth, being broken up into molecular tremors, to which we give the name of heat.

And when we reverse the process, and employ those tremors of heat to raise a weight, as is done through the intermediation of an elastic fluid in the steam-engine, a certain definite portion of the molecular motion is destroyed in raising the weight. In this sense, and this sense only, can the heat be said to be converted into gravity, or more correctly, into potential energy of gravity. It is not that the destruction of the heat has created any *new* attraction, but simply that the old attraction has now a power conferred upon it, of exerting a certain definite pull in the interval between the starting-point of the falling weight and its collision with the earth.

So also as regards magnetic attraction: when a sphere of iron

placed at some distance from a magnet rushes towards the magnet, and has its motion stopped by collision, an effect mechanically the same as that produced by the attraction of gravity occurs. The magnetic attraction generates the motion of the mass, and the stoppage of that motion produces heat. In this sense, and in this sense only, is there a transformation of magnetic work into heat. And if by the mechanical action of heat brought to bear by means of a suitable machine, the sphere be torn from the magnet and again placed at a distance, a power of exerting a pull through that distance, and producing a new motion of the sphere, is thereby conferred upon the magnet; in this sense, and in this sense only, is the heat converted into magnetic potential energy.

When, therefore, writers on the conservation of energy speak of tensions being "consumed" and "generated," they do not mean thereby that old attractions have been annihilated and new ones brought into existence, but that, in the one case, the power of the attraction to produce motion has been diminished by the shortening of the distance between the attracting bodies, and that in the other case the power of producing motion has been augmented by the increase of the distance. These remarks apply to all bodies, whether they be sensible masses or molecules.

Of the inner quality that enables matter to attract matter we know nothing; and the law of conservation makes no statement regarding that quality. It takes the facts of attraction as they stand, and affirms only the constancy of *working power*. That power may exist in the form of MOTION; or it may exist in the form of FORCE, *with distance to act through*. The former is dynamic energy, the latter is potential energy, the constancy of the sum of both being affirmed by the law of conservation. The *convertibility* of natural forces consists solely in transformations of dynamic into potential, and of potential into dynamic energy, which are incessantly going on. In no other sense has the convertibility of force, at present, any scientific meaning.

By the contraction of a muscle a man lifts a weight from the earth. But the muscle can contract only through the oxidation of its own tissue or of the blood passing through it. Molecular motion is thus converted into mechanical motion. Supposing the muscle to contract without raising the weight, oxidation would also occur, but the whole of the heat produced by this oxidation would be liberated *in the muscle itself*. Not so when it performs external work; to do that work a certain definite portion of the heat of oxidation must be expended. It is so expended in pulling the weight away from the earth. If the weight be permitted to fall, the heat generated by its collision with the earth would exactly make up for that lacking in the muscle during the lifting of the weight. In the case here supposed, we have a conversion of molecular muscular action into potential energy of gravity; and a conversion of that potential energy into heat; the heat, however, appearing at a distance from its real origin in the muscle. The

whole process consists of a transference of molecular motion from the muscle to the weight, and gravitating force is the more go-between, by means of which the transference is effected.

These considerations will help to clear our way to the conception of the transformations which occur when a wire is moved across the lines of force in a magnetic field. In this case it is commonly said we have a conversion of magnetism into electricity. But let us endeavour to understand what really occurs. For the sake of simplicity, and with a view to its translation into a different one subsequently, let us adopt for a moment the provisional conception of a mixed fluid in the wire, composed of positive and negative electricities in equal quantities and therefore perfectly neutralizing each other when the wire is still. By the motion of the wire, say with the hand, towards the magnet, what the Germans call a *Scheidungs-Kraft* a separating force—is brought into play. This force tears the mixed fluids asunder, and drives them in two currents, the one positive and the other negative, in two opposite directions through the wire. The presence of these currents evokes a force of *repulsion* between the magnet and the wire; and to cause the one to approach the other, this repulsion must be overcome. The overcoming of this repulsion is, in fact, the work done in separating and impelling the two electricities. When the wire is moved away from the magnet, a *Scheidungs-Kraft*, or separating force, also comes into play; but now it is an *attraction* that has to be surmounted. In surmounting it, currents are developed in directions opposed to the former; positive takes the place of negative, and negative the place of positive; the overcoming of the attraction being the work done in separating and impelling the two electricities.

The mechanical action occurring here is different from that occurring where a sphere of soft iron is withdrawn from a magnet, and again attracted. In this case muscular force is expended during the act of separation; but the attraction of the magnet effects the reunion. In the case of the moving wire, also we overcome a resistance in separating it from the magnet, and thus far the action is mechanically the same as the separation of the sphere of iron. But after the wire has ceased moving, the attraction ceases; and so far from any action occurring similar to that, which draws the iron sphere back to the magnet, we have to overcome a repulsion to bring them together.

There is no potential energy conferred either by the removal or by the approach of the wire, and the only power really transformed or converted, in the experiment, is muscular power. Nothing that could in strictness be called a conversion of magnetism into electricity occurs. The muscular oxidation that moves the wire fails to produce *within the muscle* its due amount of heat, a portion of that heat equivalent to the resistance overcome, appearing in the moving wire instead.

Is this effect an attraction and a repulsion at a distance? If so, why should both cease when the wire ceases to move? In fact, the deportment of the wire resembles far more that of a body moving *in*

a *resisting medium* than anything else; the resistance ceasing when the motion is suspended. Let us imagine the case of a liquid so mobile that the hand may be passed through it to and fro, without encountering any sensible resistance. It resembles the motion of a conductor in the unexcited field of an electro-magnet. Now let us suppose a body placed in the liquid, or acting on it, which confers upon it the property of *viscosity*; the hand would no longer move freely. During its motion, but then only, resistance would be encountered and overcome. Here we have rudely represented the case of the excited magnetic field, and the result in both cases would be substantially the same. In both cases heat would, in the end, be generated outside of the muscle, its amount being exactly equivalent to the resistance overcome.

Let us push the analogy a little further; suppose in the case of the fluid rendered viscous, as assumed a moment ago, the viscosity not to be so great as to prevent the formation of *ripples* when the hand is passed through the liquid. Then the motion of the hand, before its final conversion into heat, would exist for a time as wave-motion, which on subsiding would generate its due equivalent of heat. This intermediate stage, in the case of our moving wire, is represented by the period *during which the electric current is flowing through it*; but that current, like the ripples of our liquid, soon subsides, being, like them, converted into heat.

Do these words shadow forth anything like the reality? Such speculations cannot be injurious if they are enunciated without dogmatism. I do confess that ideas such as these here indicated exercise a strong fascination on my mind. Is then the magnetic field really viscous, and if so, what substance exists in it and the wire to produce the viscosity? Let us first look at the proved effects, and afterwards turn our thoughts back upon their cause. When the wire approaches the magnet, an action is evoked within it, which travels through it with a velocity comparable to that of light. One substance only in the universe has been hitherto proved competent to transmit power at this velocity; the luminiferous ether. Not only its rapidity of progression but its ability to produce the motion of light and heat, indicates that the electric current is also motion.* Further, there is a striking resemblance between the action of good and bad conductors as regards electricity, and the action of diathermanous and adiathermanous bodies as regards radiant heat. The good conductor is diathermanous to the electric current; it allows free transmission without the development of heat. The bad conductor is adiathermanous to the electric current, and hence the passage of the latter is accompanied by the development of heat. I am strongly inclined to hold the electric current, pure and simple, to be a motion of the ether

* Mr. Clerk Maxwell has recently published an exceedingly important investigation connected with this question. Even in the non-mathematical portions of the memoirs of Mr. Maxwell, the admirable spirit of his philosophy is sufficiently revealed. As regards the employment of scientific imagery, I hardly know his equal in power of conception and clearness of definition.

alone ; good conductors being so constituted that the motion may be propagated through their ether without sensible transfer to their atoms, while in the case of bad conductors this transfer is effected, the transferred motion appearing as heat.*

I do not know whether Faraday would have subscribed to what is here written ; probably his habitual caution would have prevented him from committing himself to anything so definite. But some such idea filled his mind and coloured his language through all the later years of his life. I dare not say that he has been always successful in the treatment of these theoretic notions. In his speculations he mixes together light and darkness in varying proportions, and carries us along with him through strong alternations of both. It is impossible to say how a certain amount of mathematical training would have affected his work. We cannot say what its influence would have been upon that force of inspiration that urged him on ; whether it would have daunted him, and prevented him from driving his adits into places, where no theory pointed to a lode. If so, then we may rejoice that this strong delver at the mine of natural knowledge was left free to wield his mattock in his own way. It must be admitted, that Faraday's purely speculative writings often lack that precision which the mathematical habit of thought confers. Still across them flash frequent gleams of prescient wisdom which will excite admiration throughout all time, while the facts, relations, principles, and laws which his experiments have established are sure to form the body of grand theories yet to come.

SUMMARY.

When from an Alpine height the eye of the climber ranges over the mountains, he finds that for the most part they resolve themselves into distinct groups, each consisting of a dominant mass surrounded by peaks of lesser elevation. The power which lifted the mightiest eminences, in nearly all cases lifted others to an almost equal height. And so it is with the discoveries of Faraday. As a general rule, the dominant result does not stand alone, but forms the culminating point of a vast and varied mass of inquiry. In this way, round about his great discovery of Magneto-electric Induction, other weighty labours group themselves. His investigations on the Extra Current ; on the Polar and other Condition of Diamagnetic Bodies ; on Lines of Magnetic Force, their definite character and distribution ; on the employment of the Induced Magneto-electric Current as a measure and test of Magnetic Action ; on the Revulsive Phenomena of the

* One important difference, of course, exists between the effect of motion in the magnetic field, and motion in a resisting medium. In the former case the heat is generated *in the moving conductor*, in the latter it is *in part generated in the medium*.

magnetic field, are all, notwithstanding the diversity of title, researches in the domain of magneto-electric induction.

Faraday's second group of researches and discoveries embrace the chemical phenomena of the current. The dominant result here is the great law of definite Electro-chemical Decomposition, around which are massed various researches on Electro-chemical Conduction, and on Electrolysis both with the Machine and with the Pile. To this group also belong his analysis of the Contact Theory, his inquiries as to the Source of Voltaic Electricity, and his final development of the Chemical Theory of the pile.

His third great discovery is the Magnetization of Light, which I should liken to the Weisshorn among mountains—high, beautiful, and alone.

The dominant result of his fourth group of researches is the discovery of Diamagnetism, announced in his memoir as the Magnetic Condition of all Matter, round which are grouped his inquiries on the Magnetism of Flame and Gases; on Magneto-crystalline action, and on Atmospheric Magnetism, in its relations to the annual and diurnal variation of the needle, the full significance of which is still to be shown.

These are Faraday's most massive discoveries, and upon them his fame must mainly rest. But even without them, sufficient would remain to secure for him a high and lasting scientific reputation. We should still have his researches on the Liquefaction of Gases; on Frictional Electricity; on the Electricity of the Gymnotus; on the source of power in the Hydro-electric machine, the two last investigations being untouched in the foregoing memoir; on Electro-magnetic Rotations; on Regelation; all his more purely Chemical Researches, including his discovery of Benzol. Besides these he published a multitude of minor papers, most of which, in some way or other, illustrate his genius. I have made no allusion to his power and sweetness as a lecturer. Taking him for all in all, I think it will be conceded that Michael Faraday was the greatest experimental philosopher the world has ever seen; and I will add the opinion, that the progress of future research will tend not to dim or to diminish, but to enhance and glorify the labours of this mighty investigator.

ILLUSTRATIONS OF CHARACTER.

Thus far I have confined myself to topics mainly interesting to the man of science, endeavouring, however, to treat them in a manner unrepellent to the general reader who might wish to obtain a notion of Faraday as a worker. On others will fall the duty of presenting to the world a picture of the man. But I know you will permit me to add to the foregoing analysis a few personal reminiscences and remarks, tending to connect Faraday with a wider world than that of science—namely, with the general human heart.

One word in reference to his married life, in addition to what has been already said, may find a place here. As in the former case, Faraday shall be his own spokesman. The following paragraph, though written in the third person, is from his hand :—"On the 12th of June, 1841, he married, an event which more than any other contributed to his earthly happiness and healthful state of mind. The union has continued for twenty-eight years and has in no wise changed, except in the depth and strength of its character."

Faraday's immediate forefathers lived in a little place called Clapham Wood Hall, in Yorkshire. Here dwelt Robert Faraday and Elizabeth his wife, who had ten children, one of them, James Faraday, born in 1761, being father to the philosopher. A family tradition exists that the Faradays came originally from Ireland. Faraday himself has more than once expressed to me his belief that his blood was in part Celtic, but how much of it was so, or when the infusion took place, he was unable to say. He could imitate the Irish brogue, and his wonderful vivacity may have been in part due to his extraction. But there were other qualities which we should hardly think of deriving from Ireland. The most prominent of these was his sense of order, which ran like a luminous beam through all the transactions of his life. The most entangled and complicated matters fell into harmony in his hands. His mode of keeping accounts excited the admiration of the managing board of this Institution. And his science was similarly ordered. In his *Experimental Researches*, he numbered every paragraph, and welded their various parts together by incessant reference. His private notes of the *Experimental Researches*, which are happily preserved, are similarly numbered: their last paragraph bears the figure 16,041. His working qualities, moreover, showed the tenacity of the Teuton. His nature was impulsive, but there was a force behind the impulse which did not permit it to retreat. If in his warm moments he formed a resolution, in his cool ones he made that resolution good. Thus his fire was that of a solid combustible, not that of a gas, which blazes suddenly, and dies as suddenly away.

And here I must claim your tolerance for the limits by which I am confined. No materials for a life of Faraday are in my hands, and what I have now to say, has arisen almost wholly out of our close personal relationship.

Letters of his, covering a period of sixteen years, are before me, each one of which contains some characteristic utterance;—strong, yet delicate in counsel, joyful in encouragement, and warm in affection. References which would be pleasant to such of them as still live are made to Humboldt, Biot, Dumas, Chevreul, Magnus, and Arago. Accident brought these names prominently forward; but many others would be required to complete his list of continental friends. He prized the love and sympathy of men—prized it almost more than the renown which his science brought him. Nearly a dozen years ago it fell to my lot to write a review of his "*Experimental Researches*" for the '*Philosophical Magazine*.' After he had read it, he took me by the

hand, and said, "Tyndall, the sweetest reward of my work is the sympathy and goodwill which it has caused to flow in upon me from all quarters of the world." Among his letters I find little sparks of kindness, precious to no one but myself, but more precious to me than all. He would peep into the laboratory when he thought me weary, and take me up-stairs with him to rest. And if I happened to be absent he would leave a little note for me, couched in this or some other similar form: "Dear Tyndall, —I was looking for you, because we were at tea we have not yet done will you come up?" I frequently shared his early dinner; almost always, in fact, while my lectures were going on. There was no trace of asceticism in his nature. He preferred the meat and wine of life to its locusts and wild honey. Never once during an intimacy of fifteen years did he mention religion to me, save when I drew him on to the subject. He then spoke to me without hesitation or reluctance; not with any apparent desire to "improve the occasion," but to give me such information as I sought. He believed the human heart to be swayed by a power to which science or logic opened no approach, and right or wrong, this faith, held in perfect tolerance of the faiths of others, strengthened and beautified his life.

From the letters just referred to, I will select three for publication here. I choose the first, because it contains a passage revealing the feelings with which Faraday regarded his vocation, and also because it contains an allusion which will give pleasure to a friend.

"DOVER INSTITUTION,"

"VINTNOR, ISLE OF WIGHT, 28th June, 1854.

"MY DEAR TYNDALL,

"You see by the top of this letter how much habit prevails over me; I have just read yours from thence, and yet I think myself there. However, I have left its Science in very good keeping, and I am glad to learn that you are at experiment once more. But how is the health? Not well, I fear. I wish you would get yourself strong first and work afterwards. As for the fruits, I am sure they will be good, for though I sometimes despond as regards myself, I do not as regards you. You are young, I am old.
But then our subjects are so glorious, that to work at them rejoices and encourages the feeblest; delights and enchants the strongest.

"I have not yet seen anything from Magnus. Thoughts of him always delight me. We shall look at his black sulphur together. I heard from Schonbein the other day. He tells me that Liebig is full of ozone, *i.e.* of allotropic oxygen.

"Good-bye for the present.

"Ever, my dear Tyndall,

"Yours truly,

"M. FARADAY."

The contemplation of Nature, and his own relation to her, produced in Faraday a kind of spiritual exaltation which makes itself manifest here. His religious feeling and his philosophy could not be kept apart; there was an habitual overflow of the one into the other.

Whether he or another was its exponent, he appeared to take equal delight in science. A good experiment would make him almost dance with delight. In November, 1850, he wrote to me thus: "I hope some day to take up the point respecting the magnetism of associated particles. In the mean time I rejoice at every addition to the facts and reasoning connected with the subject. When science is a republic, then it gains; and though I am no republican in other matters, I am in that." All his letters illustrate this catholicity of feeling. Ten years ago, when going down to Brighton, he carried with him a little paper I had just completed, and afterwards wrote to me. His letter is a mere sample of the sympathy which he always showed to me and my work.

"BRIGHTON, 9th Dec., 1857.

"MY DEAR TYNDALL,

"I cannot resist the pleasure of saying how very much I have enjoyed your paper. Every part has given me delight. It goes on from point to point beautifully. You will find many pencil marks, for I made them as I read. I let them stand, for though many of them receive their answer as the story proceeds, yet they show how the wording impresses a mind fresh to the subject, and perhaps here and there you may like to alter it slightly, if you wish the full idea, *i.e.* not an inaccurate one, to be suggested at first; and yet, after all, I believe it is not your exposition, but the natural jumping to a conclusion that affects or has affected my pencil.

"We return on Friday, when I will return you the paper.

"Ever truly yours,

"M. FARADAY."

The third letter will come in its proper place towards the end.

While once conversing with Faraday on science in its relations to commerce and litigation, he said to me, that at a certain period of his career, he was forced definitely to ask himself, and finally to decide, whether he should make wealth or science the pursuit of his life. He could not serve both masters, and he was therefore compelled to choose between them. After the discovery of magneto-electricity his fame was so noised abroad, that the commercial world would hardly have considered any remuneration too high for the aid of abilities like his. Even before he became so famous, he had done a little "professional business." This was the phrase he applied to his purely commercial work. His friend, Richard Phillips, for example, had induced him to undertake a number of analyses, which produced, in the year 1830, an addition to his income of more than a thousand pounds; and in 1831, a still greater addition. He had only to will it to raise in 1832 his professional business income to £5000 a year. Indeed, this is a wholly insufficient estimate of what he might, with ease, have realized annually during the last thirty years of his life.

While re-studying the *Experimental Researches* with reference to the present memoir, the conversation with Faraday here alluded to, came to my recollection, and I sought to ascertain the period when the question, "wealth or science," had presented itself with such em-

phasis to his mind. I fixed upon the year 1831 or 1832, for it seemed beyond the range of human power to pursue science as he had done during the subsequent years, and to pursue commercial work at the same time. To test this conclusion I asked permission to see his accounts, and on my own responsibility, I will state the result. In 1832, his professional business-income, instead of rising to £5000, or more, fell from £1090 4s. to £155 9s. From this it fell with slight oscillations to £92 in 1837, and to zero in 1838. Between 1839 and 1845, it never, except in one instance, exceeded £22; being for the most part much under this. The exceptional year referred to was that in which he and Sir Charles Lyell were engaged by Government to write a report on the Haswell Colliery explosion, and then his business-income rose to £112. From the end of 1845 to the day of his death, Faraday's annual professional business-income was exactly zero. Taking the duration of his life into account, this son of a blacksmith, and apprentice to a bookbinder, had to decide between a fortune of £150,000 on the one side, and his undowered science on the other. He chose the latter, and died a poor man. But his was the glory of holding aloft among the nations the scientific fame of England for a period of forty years.

The outward and visible signs of fame were also of less account to him than to most men. He had been loaded with scientific honours from all parts of the world. Without, I imagine, a dissentient voice, he was regarded as the prince of the physical investigators of the present age. The highest scientific position in this country he had, however, never filled. When the late excellent and lamented Lord Wrottesley resigned the presidency of the Royal Society, a deputation from the council, consisting of his lordship, Mr. Grove, and Mr. Cassiot, waited upon Faraday, to urge him to accept the president's chair. All that argument or friendly persuasion could do was done to induce him to yield to the wishes of the council, which was also the unanimous wish of scientific men. A knowledge of the quickness of his own nature had induced in Faraday the habit of requiring an interval of reflection, before he decided upon any question of importance. In the present instance he followed his usual habit, and begged for a little time. On the following morning I went up to his room, and said on entering, that I had come to him with some anxiety of mind. He demanded its cause, and I responded, "Lest you should have decided against the wishes of the deputation that waited on you yesterday." "You would not urge me to undertake this responsibility," he said. "I not only urge you," was my reply, "but I consider it your bounden duty to accept it." He spoke of the labour that it would involve; urged that it was not in his nature to take things easy; and that if he became president, he would surely have to stir many new questions, and agitate for some changes. I said that in such cases he would find himself supported by the youth and strength of the Royal Society. This, however, did not seem to satisfy him. Mrs. Faraday came

into the room, and he appealed to her. Her decision was adverse, and I deprecated her decision. "Tyndall," he said at length, "I must remain plain Michael Faraday to the last; and let me now tell you, that if I accepted the honour which the Royal Society desires to confer upon me, I would not answer for the integrity of my intellect for a single year." I urged him no more, and Lord Wrottesley had a most worthy successor in Sir Benjamin Brodie.

After the death of the Duke of Northumberland, our Board of Managers wished to see Mr. Faraday finish his career as President of the Institution, which he had entered on weekly wages more than half a century before. But he would have nothing to do with the presidency. He wished for rest, and the reverent affection of his friends was to him infinitely more precious than all the honours of official life.

The first requisite of the intellectual life of Faraday was the independence of his mind; and though prompt to urge obedience where obedience was due, with every right assertion of manhood he intensely sympathised. Even rashness on the side of honour found from him ready forgiveness, if not open applause. The wisdom of years, tempered by a character of this kind, rendered his counsel peculiarly precious to men sensitive like himself. I often sought that counsel, and, with your permission, will illustrate its character by one or two typical instances.

In 1855, I was appointed examiner under the Council for Military Education. At that time, as indeed now, I entertained strong convictions as to the enormous utility of physical science to officers of artillery and engineers, and whenever opportunity offered, I expressed this conviction without reserve. I did not think the recognition, though considerable, accorded to physical science in those examinations, at all proportionate to its importance; and this probably rendered me more jealous than I otherwise should have been of its claims.

In Trinity College, Dublin, a school had been organized with reference to the Woolwich examinations, and a large number of exceedingly well instructed young gentlemen were sent over from Dublin, to compete for appointments in the artillery and engineers. The result of one examination was particularly satisfactory to me; indeed the marks obtained appeared so eloquent, that I forbore saying a word about them. My colleagues, however, followed the usual custom of sending in brief reports with their returns of marks. After the results were published, a leading article appeared in 'The Times,' in which the reports were largely quoted; praise being bestowed on all the candidates, except the excellent young fellows who had passed through my hands.

A letter from Trinity College drew my attention to this article, bitterly complaining, that whereas the marks proved them to be the best of all, the science candidates were wholly ignored. I tried to set matters right by publishing, on my own responsibility, a letter in 'The Times.' The act I knew could not bear justification from

the War Office point of view; and I expected and risked the displeasure of my superiors. The merited reprimand promptly came. "Highly as the Secretary of State for War might value the expression of Professor Tyndall's opinion, he begged to say that an examiner appointed by His Royal Highness the Commander-in-Chief had no right to appear in the public papers as Professor Tyndall has done, without the sanction of the War Office." Nothing could be more just than this reproof, but I did not like to rest under it. I wrote a reply, and previous to sending it, took it up to Faraday. We sat together before his fire, and he looked very earnest, as he rubbed his hands and pondered. The following conversation then passed between us:—

F. You certainly have received a reprimand, Tyndall; but the matter is over, and if you wish to accept the reproof, you will hear no more about it.

T. But I do not wish to accept it.

F. Then you know what the consequence of sending that letter will be?

T. I do.

F. They will dismiss you.

T. I know it.

F. Then send the letter!

The letter was firm, but respectful; it acknowledged the justice of the censure, but expressed neither repentance nor regret. Faraday, in his gracious way, slightly altered a sentence or two to make it more respectful still. It was duly sent, and on the following day I entered the Institution with the conviction that my dismissal was there before me. Weeks, however, passed. At length the well-known envelope appeared, and I broke the seal, not doubting the contents. They were very different from what I expected. "The Secretary of State for War has received Professor Tyndall's letter, and *deems the explanation therein given perfectly satisfactory.*" I have often wished for an opportunity of publicly acknowledging this liberal treatment, proving, as it did, that Lord Palmerston could discern and make allowance for a good intention, though it involved an offence against routine. For many years subsequently it was my privilege to act under that excellent body, the Council for Military Education.

On another occasion of this kind, having encouraged me in a somewhat hardy resolution I had formed, Faraday backed his encouragement by an illustration drawn from his own life. The subject will interest you, and it is so sure to be talked about in the world, that no avoidable harm can arise from its introduction here.

In the year 1835, Sir Robert Peel wished to offer Faraday a pension, but that great statesman quitted office before he was able to realize his wish. The Minister who founded these pensions intended them, I believe, to be marks of honour, which even proud men might accept without compromise of independence. When, however, the intimation first reached Faraday, in an unofficial way, he wrote a letter announcing

his determination to decline the pension; and stating that he was quite competent to earn his livelihood himself. That letter still exists, but it was never sent, Faraday's repugnance having been overruled by his friends. When Lord Melbourne came into office, he desired to see Faraday; and probably in utter ignorance of the man - for, unhappily for them and us, Ministers of State in England are only too often ignorant of great Englishmen - his lordship said something that must have deeply displeased his visitor. The whole circumstances were once communicated to me, but I have forgotten the details. The term "humbug," I think, was incautiously employed by his lordship, and other expressions were used of a similar kind. Faraday quitted the Minister with his own resolves, and that evening he left his card and a short and decisive note at the residence of Lord Melbourne, stating that he had manifestly mistaken his lordship's intention of honouring science in his person, and declining to have anything whatever to do with the proposed pension. The good-humoured nobleman at first considered the matter a capital joke; but he was afterwards led to look at it more seriously. An excellent lady, who was a friend both to Faraday and the Minister, tried to arrange matters between them; but she found Faraday very difficult to move from the position he had assumed. After many fruitless efforts, she at length begged of him to state what he would require of Lord Melbourne to induce him to change his mind. He replied, "I should require from his lordship what I have no right or reason to expect that he would grant: - a written apology for the words he permitted himself to use to me." The required apology came, frank and full, creditable, I thought, alike to the Prime Minister and the philosopher.

Considering the enormous strain imposed on Faraday's intellect, the boy-like buoyancy even of his later years was astonishing. He was often prostrate, but he had immense resiliency, which he brought into action by getting away from London whenever his health failed. I have already indicated the thoughts which filled his mind during the evening of his life. He brooded on magnetic media and lines of force, and the great object of the last investigation he ever undertook was the decision of the question whether magnetic force requires *time* for its propagation. How he proposed to attack this subject we may never know. But he has left some beautiful apparatus behind; delicate wheels and pinions, and associated mirrors, which were to have been employed in the investigation. The mere conception of such an inquiry is an illustration of his strength and hopefulness, and it is impossible to say to what results it might have led him. But the work was too heavy for his tired brain. It was long before he could bring himself to relinquish it, and during this struggle he often suffered from fatigue of mind. It was at this period, and before he resigned himself to the repose which marked the last two years of his life, that he wrote to me the following letter, - one of many priceless letters now before me, - which reveals more than anything another pen could express, the state of his mind at the time. I was some-

times censured in his presence for my doings in the Alps, but his constant reply was, "let him alone, he knows how to take care of himself." In this letter, anxiety on this score reveals itself, for the first time.

"HAMPTON COURT, 1st Aug., 1864.

"MY DEAR TYNDALL,

"I do not know whether my letter will catch you, but I will risk it though feeling very unfit to communicate with a man whose life is as vivid and active as yours; but the receipt of your kind letter makes me to know that though I forget, I am not forgotten, and though I am not able to remember at the end of a line what was said at the beginning of it, the imperfect marks will convey to you some sense of what I long to say. We had heard of your illness through Miss Moore, and I was therefore very glad to learn that you are now quite well; do not run too many risks, or make your happiness depend too much upon dangers, or the hunting of them. Sometimes the very thinking of you and what you may be about wears me with fears, and then the cogitations pause and change, but without giving me rest. I know that much of this depends upon my own worn-out nature, and I do not know why I write it, save that when I write to you I cannot help thinking it, and the thoughts stand in the way of other matter.

* * * * *

"See what a ~~rather~~ desultory epistle I am writing to you, and yet I feel so weary that I long to leave my desk and go to the couch.

"My dear wife and Jane desire their kindest remembrances, I hear them in the next room; . . . I forget—but not you, my dear Tyndall, for I am

"Ever yours,

"M. FARADAY."

This weariness subsided when he relinquished his work, and I have a cheerful letter from him, written in the autumn of 1865. But towards the close of that year he had an attack of illness, from which he never completely rallied. He continued to attend the Friday Evening Meetings, but the advance of infirmity was apparent to us all. Complete rest became finally essential to him, and he ceased to appear amongst us. There was no pain in his decline to trouble the memory of those who loved him. Slowly and peacefully he sank towards his final rest, and when it came, his death was a falling asleep. In the fulness of his honours and of his age he quitted us; the good fight fought, the work of duty—shall I not say of glory—done. The "Jane" referred to in the foregoing letter is Faraday's niece, Miss Jane Barnard, who with an affection raised almost to religious devotion, watched him and tended him to the end.

I saw Mr. Faraday for the first time on my return from Marburg in 1850. I came to the Royal Institution, and sent up my card with a copy of the paper which Knoblauch and myself had just completed. He came down and conversed with me for half-an-hour. I could not fail to remark the wonderful play of intellect and kindly feeling exhibited by his countenance. When he was in good health the question of his age would never occur to you. In the light and laughter of his eyes you never thought of his gray hairs. He was

then on the point of publishing one of his papers on magno-crystalline action, and he had time to refer in a flattering note to the memoir I placed in his hands. I returned to Germany, worked there for nearly another year, and in June, 1851, came back finally from Berlin to England. Then, for the first time, and on my way to the meeting of the British Association, at Ipswich, I met a man who has since made his mark upon the intellect of his time, who has long been, and who by the strong law of natural affinity must continue to be a brother to me. We were both without definite outlook at the time, needing proper work, and only anxious to have it to perform. The chairs of Natural History and of Physics being advertised as vacant in the University of Toronto, we applied for them, he for the one, I for the other; but, possibly guided by a prophetic instinct, the University authorities declined having anything to do with either of us. If I remember aright, we were equally unlucky elsewhere.

One of Faraday's earliest letters to me had reference to this Toronto business, which he thought it unwise in me to neglect. But Toronto had its own notions, and in 1853, at the instance of Dr. Bence Jones, and on the recommendation of Faraday himself, a chair of physics at the Royal Institution was offered to me. I was tempted at the same time to go elsewhere, but a strong attraction drew me to his side. Let me say that it was mainly his and other friendships, precious to me beyond all expression, that caused me to value my position here more highly than any other that could be offered to me in this land. Nor is it for its honour, though surely that is great, but for the strong personal ties that bind me to it, that I now chiefly prize this place. You might not credit me were I to tell you how lightly I value the honour of being Faraday's successor compared with the honour of having been Faraday's friend. His friendship was an energy and inspiration; his "mantle" is a burden almost too heavy to be borne.

Sometimes during the last year of his life, by the permission or invitation of Mrs. Faraday, I went up to his rooms to see him. The deep radiance, which in his time of strength flashed with such extraordinary power from his countenance, had subsided to a calm and kindly light, by which my latest memory of him is warmed and illuminated. I knelt one day beside him on the carpet and placed my hand upon his knee, he stroked it affectionately, smiled, and murmured, in a low, soft voice, the last words that I remember as having been spoken to me by Michael Faraday.

It was my wish and aspiration to play the part of Schiller to this Goethe; and he was at times so strong and joyful,—his body so active, and his intellect so clear,—as to suggest to me the thought that he, like Goethe, would see the younger man laid low. Destiny ruled otherwise, and now he is but a memory to us all. Surely no memory could be more beautiful. He was equally rich in mind and heart. The fairest traits of a character sketched by Paul, found in him perfect illustration. For he was "blameless, vigilant, sober, of good behaviour, apt to teach, not given to filthy lucre." He had not

a trace of worldly ambition, he declared his duty to his Sovereign by going to the levee once a year, but beyond this he never sought contact with the great. The life of his spirit and of his intellect were so full, that the things which men most strive after were absolutely indifferent to him. "Give me health and a day," says the brave Emerson, "and I will make the pomp of emperors ridiculous." In an eminent degree Faraday could say the same. What to him was the splendour of a palace compared with a thunderstorm upon Brighton Downs?—what among all the appliances of royalty to compare with the setting sun? I refer to a thunderstorm and a sunset, because these things excited a kind of ecstasy in his mind, and to a mind open to such ecstasy the pomps and pleasures of the world are usually of small account. Nature, not education, rendered Faraday strong and refined. A favourite experiment of his own was representative of himself. He loved to show that water in crystallizing excluded all foreign ingredients, however intimately they might be mixed with it. Out of acids, alkalis, or saline solutions, the crystal came sweet and pure. By some such natural process in the formation of this man, beauty and nobleness coalesced, to the exclusion of everything vulgar and low. He did not learn his gentleness in the world, for he withdrew himself from its culture; and still this land of England contained no truer gentleman than he. Not half his greatness was incorporated in his science, for science could not reveal the bravery and delicacy of his heart.

But it is time that I should end these weak words, and lay my poor garland on the grave of this

"Just and faithful knight of God."

[J. T.]

Friday, February 14, 1868.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

HENRY E. ROSCOE, B.A. F.R.S.

On Vanadium, one of the Trivalent Group of Elements.

THE metal vanadium (so called from Vanadis, a cognomen of the Scandinavian goddess Freia) was discovered in 1830 by Sefstrom in the celebrated Swedish bar-iron made from the Taberg ore. From this source, even when using many pounds of the iron, Sefstrom obtained only minute quantities of the new substance, but he found it in somewhat larger amount in the slag or cinder produced in the reduction of the iron ore. Sefstrom ascertained some of the most peculiar characters of the substance, proved it to be a new element, and prepared some of its compounds in the pure state. The reactions by which vanadium can be separated and distinguished from all the other elements are: (1) The formation of a soluble sodium vanadate when the vanadium compounds are fused with sodium carbonate; (2) the formation of an insoluble ammonium vanadate when sal-ammoniac is added to the solution of a soluble vanadate; (3) the production of a splendid blue solution when this ammonium salt, dissolved in hydrochloric acid, is warmed with reducing agents such as oxalic acid.

Sefström not having leisure to prosecute the full examination of the properties of the new metal, handed over his preparations to Berzelius; and it is to the investigations of the great Swede (1831) that we owe almost all our acquaintance with the chemistry of vanadium.

Since Berzelius's time vanadium has been discovered in many minerals, of which a lead-ore containing lead vanadate and called by the mineralogists vanadinite, is the most important. It has also been found in many iron ores, in clay, bricks, and even in caustic soda. Still the quantity of the substance found in all these various sources has been extremely small; so much so, that the vanadium compounds must be reckoned amongst the greatest of chemical rarities, and we find them quoted in the price lists of dealers in chemicals at 1s. 6d. per grain, or 35s. per ounce! It is clear that our knowledge of the chemical properties of a substance so rare must necessarily be but incomplete, as the difficulties of obtaining exact or satisfactory results with small quantities of material are evident; and, in fact, the statements of the only persons who have worked upon the subject re-

cently (Schafarik Czudnowicz), instead of giving us any more reliable information respecting the character of vanadium, have only served to throw doubt upon some of the conclusions of Berzelius, and thus to render our knowledge even less complete than it appeared to be.

Hence it was with much satisfaction that, in February, 1865, the speaker came into possession of a plentiful source of vanadium in a by-product obtained in the preparation of cobalt from the copper-bearing beds of the lower Keuper Sandstone of the Trias at Alderley Edge, in Cheshire. The manager of the works was puzzled to know why a blue solution, supposed by him to contain copper, did not deposit the red metal upon a strip of zinc; the speaker recognized this reaction as due to the presence of vanadium, and secured the whole of the by-product, which he found to contain about 2 per cent. of the rare metal. The exact position of the vanadium mineral in the sandstone beds cannot now be stated, as the mine (at Mottram St. Andrews) from which the cobalt ore was obtained is now closed, and cannot be entered. The general characters of the deposit are, however, well known, and exhibit points of great interest; they have been well described by Mr. Hull as follows:—

“The ‘edge’ or escarpment of Alderley rises from the eastern side of the plain of Cheshire gradually towards the east, but with a steep and abrupt ridge towards the north. This northern bank is richly wooded, and has a very beautiful aspect when viewed from a distance, as it contrasts strongly with the almost level plain which sweeps away to the northward and westward from its base. The ridge has here been upheaved along the line of a large fault, bearing east and west, throwing down at its base the Red Marl; and on the other side bringing up the soft sandstone of the Bunter, capped by a mural cliff of lower Keuper Conglomerate, which often breaks out in conspicuous masses through the foliage. The beds rise from the plain towards the east at an angle of about from 5° to 10°, and the escarpment is continued southward for some distance facing the east.”

SUCCESSION OF BEDS IN DESCENDING ORDER—(Hull).

Red Marl		Red and grey laminated Marls, Brownish flaggy Sandstones and Marls.
Waterstones	Lower Keuper Sandstone, 500 feet.	White and brown Freestone.
Freestone		Soft white, yellow, and varie- gated Sandstone.
Copper-bearing Sandstone ..		Hard quartzose Conglomerate, underlain by bands of Marl, forming the base of the Keuper Sandstone.
Conglomerate		
Upper red and mottled Sand- stone	Bunter.	Soft fine-grained yellow and red Sandstone, being the uppermost member of the Bunter Sandstone.

The beds in the above series which claim the greatest share of our attention are those at the base of the Keuper series, for in these

occur the copper and other minerals. The copper, as both blue and green carbonate, occurs disseminated throughout the sand, the ore coating the outside of the grains of sand and the pebbles of quartz. In addition to copper, bands containing lead both as carbonate and sulphide (galena) occur, also bands and veins of cobalt ochre, oxide of manganese, and iron ochre in workable quantity. The copper is extracted from the ore by solution in hydrochloric acid and precipitation as metal by scrap iron. The ordinary copper liquor, as well as the oxide of iron precipitated by lime from the solution of the chloride, does not contain any trace of vanadium, nor was the speaker able to detect any of this metal in the ore as at present worked.

Following, in the main, the process of preparation adopted by Sefstrom, the speaker obtained from the above-mentioned lime precipitate several pounds of pure ammonium vanadate, from which all the other compounds of vanadium can be prepared.

What now were the conclusions to which Berzelius arrived from his experiments concerning the constitution of the vanadium compounds? He corroborated Sefstrom's statement, that the most characteristic feature of the substance is the existence of an acid-forming oxide, termed vanadic acid, produced whenever any of the oxides are heated in the air. Berzelius also discovered two other oxides of vanadium, of which he ascertained the composition; and likewise a volatile chloride. To the highest oxide he gave the formula VO_3 , to the second VO_2 , and to the lowest (or suboxide) VO ; whilst the chloride was represented by VCl_3 . The atomic weight of the metal he ascertained to be $\text{V} = 68.5$. Berzelius came to this conclusion from the following experimentally ascertained facts: (1) That on passing hydrogen over heated vanadic acid a constant loss of weight occurred, and the suboxide was formed; (2) that when dry chlorine is passed over the suboxide thus prepared, the volatile chloride was formed, and a residue of vanadic acid remained, which was exactly equal in weight to one-third of the acid originally taken for reduction. Hence assuming that the lowest oxide contains one atom of oxygen (an assumption borne out by the analysis of the chloride), the acid must contain three atoms of oxygen,* and the following formulæ represent the composition of these compounds according to Berzelius:—

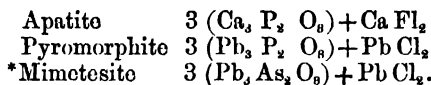


The interest attaching to the conclusions which Berzelius fairly drew from his experiments was much heightened by an observation made by Rammelsberg in 1856, as to the exact crystalline form of the mineral vanadinite, a double salt of lead vanadate and lead chloride.

So long ago as 1780 Werner had observed the identity of crystalline form of two minerals, *viz.* apatite, a phosphato-fluoride of cal-

* Berzelius concludes that the acid does not contain two atoms of metal, inasmuch as no alum could be formed with potassium sulphate corresponding to those formed by well-known sesquioxides.

cium, and pyromorphite, a phosphato-chloride of lead; to which may be added, mimetesite, an arsenato-chloride of lead. These minerals all have an analogous composition, being represented by the formulæ—



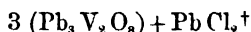
They are truly isomorphous, crystallizing in hexagonal prisms, terminated with hexagonal pyramids, having the same angles and the same length of axes. Rammelsberg added to this list the mineral vanadinite, which he ascertained by measurement to be strictly isomorphous with the foregoing, and to be as follows. The angle P on P was in

1) Vanadinite .	142° 30'	3) Pyromorphite	142° 15'
2) Apatite . .	142° 20'	4) Mimetesite .	142° 7'

and the relation of the length of the axis :

1) 1 :	0.727	3) 1 :	0.736
2) 1 :	0.732	4) 1 :	0.739.

So far, indeed, has the identity of crystalline form been traced, that crystals have been found which at one end consisted of vanadinite, and at the other of pyromorphite (Heddle). Now judging from the crystallographic analogies alone, we should conclude that the formula of vanadinite is

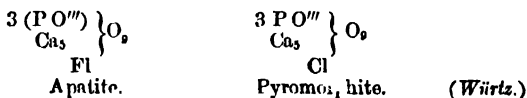


the oxide of vanadium contained in the mineral having a formula $\text{V}_2 \text{O}_5$, agreeing with the corresponding oxides of phosphorus and arsenic, $\text{P}_2 \text{O}_5$ and $\text{As}_2 \text{O}_5$. In making this assumption, we are, however, at once confronted with the unyielding chemical facts of Berzelius, according to which the oxide in question must be represented by the formula VO_2 , and contains three, and not five, atoms of oxygen.

It is, then, evident that we have here either to do with an exception to the law of Isomorphism, or else Berzelius's views are erroneous. Until this latter has been proved to be the case, chemists have, however, only been justified in assuming the former alternative to be the correct explanation.

The speaker stated that in order to endeavour to clear up this question, he had most carefully repeated Berzelius's experiments, and

*This group of minerals may be considered as Calcium Triphosphofluorhydine, &c., thus:—



† Or Lead Trivanadochlorhydine $3 (\text{V O} \text{ Pb}_3 \text{ Cl}) \}$

that he had confirmed them in every particular; but having pursued the subject further than Berzelius, he had at last come to conclusions concerning the constitution of the vanadium compounds totally different from those drawn by the Swedish chemist, and had succeeded in obtaining the key to the enigma presented by the above anomalous crystallographic relations.

The speaker has proved that the substance supposed by Berzelius to be Vanadium, $V=68.5$, is not the metal, but an oxide, and that the true atomic weight of the metal is $68.5-16=52.5$ (or rather, according to the speaker's exact determinations of the atomic weight, $67.3-16=51.3$).^{*} The highest oxide, the vanadic acid, VO_3 , of Berzelius, hence becomes a pentoxide, V_2O_5 , corresponding to P_2O_5 , and As_2O_5 , and the isomorphism of vanadinite with the pyromorphite group of minerals is fully explained. The suboxide of Berzelius is a tri-oxide, V_2O_3 , whilst the tetrachloride (VCl_4) of Berzelius is an oxychloride, having the formula $VOCl_3$, and corresponding to oxychloride of phosphorus, $POCl_3$. The oxide supposed by Berzelius to be the metal contains 51.3 parts by weight of vanadium to 16 parts by weight of oxygen, and the vanadic oxide of Berzelius also exists, containing 51.3 parts of the metal to 32 parts of oxygen; to these oxides the empirical formulæ V_2O_2 and V_2O_4 may be given. Thus we have the following as representing the true composition of these vanadium compounds:—

	Dioxide.	Trioxide.	Tetroxide.	Pentoxide	Oxytrichloride.
$V=51.3$	V_2O_2	V_2O_3	V_2O_4	V_2O_5	$VOCl_3$

Each of the four oxides can be obtained in the anhydrous state; the dioxide is obtained as a grey metallic powder, by passing the vapour of the oxytrichloride mixed with hydrogen over red-hot carbon. The trioxide is obtained by the reduction of vanadic acid in a current of hydrogen, and the tetroxide is formed by the slow oxidation of the trioxide.

The lowest or dioxide of vanadium (V_2O_2) is obtained in solution by the reducing action of nascent hydrogen evolved from zinc, cadmium, or sodium amalgam upon the sulphuric acid solution of vanadic acid, which, passing through all stages of blue and green colour, ultimately assumes a permanent lavender tint. This solution of V_2O_2 in sulphuric acid acts as a most powerful reducing agent, bleaching indigo solution and other vegetable colouring matters as rapidly as chlorine;

^{*} In his paper on Vanadium, read before the Royal Society (Dec. 19, 1867), the author ventured to predict that the difference between the number he obtained (67.3) and that found by Berzelius (68.5) was probably owing to the fact that the vanadium compounds employed by Berzelius contained traces of phosphorus, which render the perfect reduction of the vanadic acid in hydrogen impossible. Most fortunately this supposition has been singularly verified, inasmuch as Dr. Frankland has kindly placed in the speaker's hands a small specimen of vanadate of ammonia found in Faraday's collection, and labelled, "Sent to me by Berzelius, 1831." On examination, this sample was found to contain considerable quantities of phosphorus, thus confirming the speaker's previously expressed opinion.

it also absorbs oxygen with avidity from the air, forming a deep brown solution. The other oxides of vanadium may be obtained in solution by the action of various reducing agents on the sulphuric solution of vanadic acid. Thus, by the action of nascent hydrogen evolved from magnesium a permanent *green* tint is obtained, and the vanadium is contained in solution as the trioxide, V_2O_3 ; whilst if moderate reducing agents, such as sulphurous acid, sulphuretted hydrogen, or oxalic acid are employed, the colour of the liquid does not pass beyond the *blue* stage, and the vanadium is contained in solution as tetroxide, V_2O_4 .* The different colours of solutions containing these oxides was exhibited by means of the magnesium light.

The fact that the lemon-coloured chloride (the terchloride of Berzelius) contains oxygen was clearly demonstrated during the discourse by passing the vapour from a few grammes of the substance, together with perfectly pure hydrogen gas, over red-hot carbon. A portion of the oxygen of the oxychloride unites with the carbon to form carbonic acid, and the presence of this gas was shown by the precipitation of barium carbonate in clear baryta water contained in two test-tubes placed one before the other. At the commencement of the experiment, the carbonic acid was entirely absorbed by the small quantity of baryta water contained in the first test-tube; but after some time the hydrochloric acid gas simultaneously produced by the decomposition of the chloride saturated this liquid, expelling the carbonic acid gas, which being carried forward into the second test-tube, threw down a bulky precipitate of barium carbonate, thus showing that the turbidity cannot possibly be due to the presence of any vanadium compound. It was found quite unnecessary to place a tube containing heated copper oxide after the red-hot carbon, for the purpose of oxidizing any carbonic oxide gas which might be formed, inasmuch as carbonic acid was always left in sufficient quantity to give a considerable precipitate. No method has been found for separating the whole of the oxygen from the oxychloride, and hence it has been impossible to make the above experiment quantitatively. Solid oxychlorides are obtained by the action of hydrogen upon the oxytrichloride, one of which resembles mosaic gold, possessing a bright metallic bronze-like lustre, and having been taken for the metal by Schafarik.

The atomic weight of vanadium was determined (1) by reducing the pentoxide to trioxide in a current of hydrogen. (2) By the

* In his communication to the Royal Society (Bakerian Lecture, Proc. Royal Soc., XVI., 220), the author gave the empirical formula VO and VO_2 to the 1st and 3rd oxides of vanadium, as the molecular weights of these oxides have not been determined, and it is uncertain whether they obey the law of even atomicities, or, like the only corresponding compounds, the nitrogen oxides, are exceptions to this law.

On consideration, the author has, however, thought it best to adopt the doubled formula as urged by Sir Benjamin Brodie on the occasion above referred to.

analysis of the oxytrichloride. The atomic weight obtained as the mean of a large number of well-agreeing experiments is 51·3.

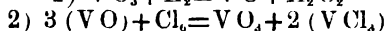
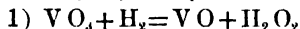
The metal itself has not yet been obtained, but a compound of vanadium and nitrogen has been prepared, shown by direct analysis to contain 14 parts by weight of nitrogen to 51·3 parts by weight of vanadium, corresponding to the formula VN . The existence of this compound is proof positive of the true atomic weight of the metal, and the nitride serves as the point of departure from which to seek for the metal and the true chlorides of vanadium, one of which, VCl_3 , has already been prepared by the action of chlorine upon the nitride. It is a dark brown liquid, which decomposes when thrown into water, forming a green solution containing V_2O_3 . The speaker demonstrated the fact that the oxychloride, $VOCl_3$, when thrown into water decomposes with formation of a *yellow* solution of vanadium pentoxide, V_2O_5 , whilst the trichloride, VCl_3 , on being similarly treated yields a *green* solution containing the metal in solution as trioxide, V_2O_3 . He then compared these reactions with the decomposition of the corresponding phosphorus compounds, $POCl_3$ and PCl_3 , forming P_2O_5 and P_2O_3 , and rendered these reactions visible by obtaining a precipitate of yellow silver phosphate in the first case, and of black metallic silver in the second.

The characters of the vanadates themselves bear out the analogy of the highest oxide with the corresponding oxides of phosphorus and arsenic. In the first place, all the naturally occurring vanadates are tribasic; secondly, the true character of vanadic acid is shown to be tribasic, by the fact that, when the pentoxide is fused with sodium carbonate, three atoms of CO_2 are liberated, and the normal or ortho-vanadate, $Na_3V_2O_8$ (corresponding to $Na_3P_2O_8$), is formed; thirdly, the so-called mono vanadates are monobasic salts, corresponding to the monobasic phosphates, and may be termed meta-vanadates, thus, $NaVO_3$ and Ba_2VO_3 , whilst the so-called bi-vanadates are anhydro-salts.

All the reactions by which Berzelius explained the facts he discovered, can equally well be represented according to the new atomic weight and constitution; thus:—

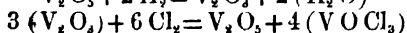
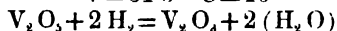
BERZELIUS' FORMULÆ.

$$V = 68\cdot5 \quad O = 8$$



NEW FORMULÆ.

$$V = 51\cdot3 \quad O = 16$$



The speaker stated that the foregoing facts clearly pointed out that vanadium, hitherto standing in no definite relation to other elements, must be regarded as a member of the well-known Trivalent

or Triad class of elementary substances, comprising nitrogen, phosphorus, boron, arsenic, antimony, and bismuth.

It is true that we are still but imperfectly acquainted with many of the characters of vanadium, but the more its nature is studied, the more points of family resemblance will be discovered, and the more close will the ties be found, which bind it to the great Triad family.

The following tabular statement of the compounds of the most important members of this group clearly shows their common relations:—

TRIVALENT GROUP OF ELEMENTS.

	Nitrogen	Phosphorus.	Vanadium.	Arsenic.	Antimony.
	N = 14	P = 31	V = 51·3	As = 75	Sb = 122
Trihydrides	N H ₃	P H ₃	—	As H ₃	Sb H ₃
Trichlorides	N Cl ₃ (?)	P Cl ₃	V Cl ₃	As Cl ₃	Sb Cl ₃
Pentachlorides	—	P Cl ₅	—	—	Sb Cl ₅
Oxychlorides	—	P O Cl ₃	V O Cl ₃	—	—
Monoxides	N ₂ O	—	—	—	—
Dioxides	N ₂ O ₂	—	V ₂ O ₃	—	—
Trioxides	N ₂ O ₃	P ₂ O ₃	V ₂ O ₃	As ₂ O ₃	Sb ₂ O ₃
Tetroxides	N ₂ O ₄	—	V ₂ O ₄	—	Sb ₂ O ₄
Pentoxides	N ₂ O ₅	P ₂ O ₅	V ₂ O ₅	As ₂ O ₅	Sb ₂ O ₅

In conclusion, the speaker remarked that vanadium was the fourth substance, supposed by its discoverer to be a metal, which had in recent years been shown to be a compound body.

<i>Titanium.</i>	<i>Uranium.</i>	<i>Niobium.</i>	<i>Vanadium.</i>
Wollaston, 1823.	Klaproth, 1789.	{ Hatchett, 1801.	{ Sefstrom and
Wohler, 1849.	Pelagot, 1849.	{ Rose, 1842-64.	{ Berzelius, 1831.
		Magnac, 1865.	

[H. E. R.]

Friday, February 28, 1868.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

A. VERNON HARCOURT, Esq. M.A.
SECRETARY OF THE CHEMICAL SOCIETY.

On the Rate at which Chemical Actions take place.

THE science of Chemistry may be defined as the science which investigates the relations of the different kinds of matter one to another. The conception of different kinds of matter, -each of which has its particular character, its own colour and crystalline form, its own hardness and brittleness or the reverse, its own conducting powers, its own specific heat and specific gravity, and many other peculiarities of its own, and each of which is homogeneous, the smallest particle having all these properties equally with the largest mass,—is the fundamental conception of Chemistry.

And the whole world to a chemist is only a mixture of such different kinds of matter, whose mode of aggregation has been and is being determined by physical and vital forces which are foreign to his science, but whose resemblances and differences, and whose changes under changed conditions or by contact one with another, form the subject of his study.

In the study of any chemical change there are two things to be discovered: first, the *result* of the change,—what kinds of matter have ceased to exist and what have come into existence; and secondly, the *course* of the change; as to which such inquiries as the following present themselves,—at what rate does the change occur, and under what conditions? Is it simple, or does it consist of several changes? Are these dependent or independent, successive or simultaneous?—with many others of a more hypothetical kind as to the molecular nature of the change. A familiar example of this twofold nature of chemical inquiry may be drawn from the case of a fire, a chemical change which has been more watched than any other. We know all that is to be known as to the result of the change, when we have discovered that the coals are a mixture of various hydrocarbons with a small quantity of metallic salts, that the air is a mixture of oxygen and nitrogen, and that when the fire has burnt out, there exists, instead of so much coal and so much air, a quantity of carbonic acid and water, the salts, which form the ash, and the nitrogen remaining mainly as they were. But there is still much besides this to be found out as to the burning of the fire. How, for example, is the rate at which it burns affected by the

draught, or by the density of the air, or by the breaking up of the fuel, or by access of the sun's rays? What are the substances, formed from the heated coal, which actually burn? Does the reduction of the products of combustion by carbon play an important part in the phenomenon? Such questions as these relate to the course of the chemical change.

The two lines of inquiry thus indicated have been pursued with very unequal vigour. The study of the results of chemical action has engrossed the attention of chemists almost to the exclusion of the study of their course. And, indeed, so great is the number of different kinds of matter, all capable of undergoing a multitude of changes by the action of heat or electricity or by contact with others, giving rise thus to new kinds of matter capable of similar changes, that this part of the science appears absolutely boundless. The direction which chemistry has taken in consequence of this superabundance of materials may, perhaps, be contrasted with that taken by physical science. If the number of distinct physical forces met with in nature, such as gravity, magnetism, electricity, heat, light, &c., instead of being quite a small number, had been a large number, and these forces had proved to be convertible not only one into another but into an infinite variety of other distinct forces, physical experimentalists might have occupied themselves wholly with establishing the transmutations of one kind of force into another and creating new modes of force, instead of studying minutely, as they have done, the conditions under which the existing forces are produced, and the laws which govern their distribution and transformation.

It is, however, not only the vastness of the chemical field, and the particular satisfaction which so solid a result as the creation of a new kind of matter brings to the mind of the investigator, which has led to the neglect of the study of the course of chemical changes. This study is beset with peculiar difficulties, and indeed, out of the vast number of chemical changes whose results are known, there are but very few whose course can readily be observed. The principal reason of this is the velocity with which such changes take place; and this velocity is apt to be the greatest in the case of the simple chemical actions which are most suitable for investigation. Either, then, we must contrive some mode of estimating a very great velocity, as has been done for the measurement of the rate at which light and electricity travel, or we must select a change—and this the variety of chemistry makes possible—which proceeds at a rate convenient for observation.

Examples of the different velocity of chemical changes are furnished by the precipitation of a barium and of a calcium salt from their solutions upon the addition of a sulphate. With the former, the change is apparently instantaneous. The result is known, but the course cannot be observed. With the latter, the change is gradual, and it would be possible to determine its rate at different temperatures and with different quantities of the two salts in solution.

The decomposition of a hyposulphite in an acid solution is another example of a gradual, observable change.

We may compare, also, the reduction of a chromate by a sulphite and by an oxalate. The former occupies no appreciable time; the actual time is, doubtless, greater in a more dilute solution and at a lower temperature, but we cannot discern any difference. But with an oxalate for reducing agent, though the final result of the change is the same, the action takes a long time to accomplish itself, and it would be quite practicable to observe in what way different circumstances affect its rate.

But in order to discover the laws which govern the rate of any chemical change, some exact mode of measuring the rate is necessary. It remains to show how this may be accomplished in certain cases.

A solution of ammonium nitrite, heated to a temperature of about 80° C. in a flask provided with a gas delivery tube, gives off a quantity of nitrogen, which may be collected over the pneumatic trough. By keeping the temperature constant, and collecting the gas evolved during successive equal intervals of time in similar cylinders, it is possible at once to show the regular diminution in the volume of gas which is caused by the constant diminution of the quantity of salt in solution. And by making the experiment and measuring the quantities of gas with accuracy, it would be possible to discover the relation between the amount of change going on at any moment and the amount of salt in solution, and also, by making the experiment at different temperatures, to discover how the temperature of the solution affects the rate at which the action takes place.

The reduction of a permanganate by an oxalate in an acid solution furnishes another case of a gradual measurable change, and has been more fully studied. Here it is possible to start the change at any moment by adding the measured quantity of permanganate to the other ingredients and mixing rapidly. It is also possible to stop it at any moment by adding a solution of iodide to the mixture; and the iodine which is set free by the action of the residual permanganate corresponds to it in quantity and can readily be estimated. By making a number of such experiments, differing from one another only in the time during which the gradual change is allowed to proceed, its course may be traced throughout with any required degree of minuteness. The results obtained in many series of such experiments are given in the 'Philosophical Transactions for 1866,' p. 206. The general conclusion to which they lead is that the total amount of change occurring at any moment is directly proportional, all other conditions being alike, to the amount of permanganate in the solution.

The last chemical change which has been investigated from this point of view, is that which takes place when dilute acid solutions of an iodide and a dioxide, such as barium or sodium dioxide, are mixed together. By arranging suitably the dilution, acidity, and temperature of the solution, the change may be made to proceed at any rate that is most convenient for measurement. One of the products of the

change is iodine, a substance for which we have, in its action on starch, a most delicate test. By bringing a small known quantity of hyposulphite into the liquid, all the iodine that is formed by the gradual reaction of peroxide and iodide is reconverted into iodide, and this continues till iodine enough has been formed to remove all the hyposulphite. As soon as the last particle of hyposulphite has been removed (converted into tetrathionate), free iodine appears in the solution, and the moment of its appearance may be noted by carefully watching the colour of the liquid. By adding successive quantities of hyposulphite, and observing the interval which elapses between successive reappearances of the blue colour of the iodide of starch, it is possible accurately to determine the rate at which the change is proceeding. An account of a number of experiments made in this way, and of their results, is to be found in the 'Philosophical Transactions for 1867,' p. 117. Each set of observations determines at what rate the dioxide is reduced under certain definite conditions; and by making different series of experiments, in which the several conditions affecting the rate of change are systematically varied, it is possible to discover the laws of connection between each of the conditions and the amount of change. Having discovered these laws, our knowledge of the change is so far complete, and we can predict with certainty the time that would be required for any given amount of change under any given circumstances.

The following propositions embody the principal conclusions to which the examination of these cases of gradual chemical change has led:—

1. The rate at which a chemical change proceeds is constant under constant conditions, and is independent of the time that has elapsed since the change commenced.

2. When any substance is undergoing a chemical change, of which no condition varies, excepting the diminution of the changing substance, the amount of change occurring at any moment is directly proportional to the quantity of the substance.

3. When two or more substances act one upon another, the amount of action at any moment is directly proportional to the quantity of each of the substances.

4. When the rate of any chemical change is affected by the presence of a substance, which itself takes no part in the change, the acceleration or retardation produced is directly proportional to the quantity of the substance.

5. The relation between the rate of a chemical change occurring in a solution, and the temperature of the solution, is such, that for every additional degree the number expressing the rate is to be multiplied by a constant quantity.

[A. V. II.]

Friday, April 24, 1868.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

J. H. GLADSTONE, Ph.D. F.R.S.

On some New Experiments on Light.

THE speaker commenced by referring to the fact that we are constantly making new experiments or observations on light: in fact, all seeing is but a comparison of different degrees of light and shade, and the contrast of colours. Most of the rays that meet our eyes from surrounding objects are reflected rays, but some of the commonest things, such as the water-bottles and tumblers of cut-glass on our dining tables, exhibit beautifully the bending, the magnifying, the diminishing, and the production of coloured fringes, due to refraction. The purpose of this discourse was to rise from the simplest phenomena of this kind to a consideration of Refraction-equivalents, and to describe the state of our present knowledge in regard to them.

By means of the electric lamp it was shown that a piece of glass, or other transparent body, will throw a perfectly black shadow if the two surfaces through which the ray passes be not parallel; that the light is then bent on one side, and at the same time spread out into its component colours; that this bending (refraction) varies with the amount of inclination of the two surfaces to one another, but in such a way that the sine of the angle of refraction bears a constant ratio to the sine of the angle of incidence; that this constant number, termed the index of refraction, or μ , belongs only to the one substance, each solid, liquid, or gas having its own index; that there is no necessary connection between the amount of refraction and the length of the spectrum (dispersion) caused by different substances, whether gaseous, liquid, or solid—for instance, a solution of an iodide always disperses more than a solution of the chloride of the same metal, even though it be diluted to the same amount of refraction.

This index of refraction is affected by change of temperature. In liquids, and probably in all gases, the bending decreases as the thermometer rises; in solids, on the contrary, as lately shown by Fizeau, the change is in the opposite direction, crown glass always remaining the same, and fluor spar being the only case where he observed a diminution. This was experimentally demonstrated in regard to liquids. Thus a yellow sodium ray, which had passed through a hollow prism filled with oil of nutmeg, and thence through another filled with bisulphide of carbon, moved some inches along the screen, when the nutmeg oil was warmed a few degrees by stirring it with heated iron

wire. This index of refraction is still more materially affected when a body passes from the solid to the liquid, or from the liquid to the gaseous condition; a fact that was illustrated by the visibility of the water melted in crystalline spaces in the middle of a block of ice.

The index of refraction of a mixture is moreover not always the mean of the indices of its constituents. Thus a ray passed successively through two hollow prisms filled with equal quantities of alcohol and water respectively, fell on the screen in a certain position; but when the two liquids were mixed together, and divided between the two prisms, the ray was visibly refracted to a greater distance.

These changes depend on the alterations of volume which the substances undergo; and the speaker, in conjunction with the Rev. T. Pelham Dale, had observed in liquids that the index of refraction, minus unity, divided by the density (in symbolic language $\frac{\mu-1}{d}$) is constant for all temperatures, and for all mixtures, or rather that the coincidence is very close but not quite perfect on account of some other law not yet understood. This conclusion has been abundantly verified by Landolt of Bonn, Ketteler, and Wullner, and the former experimenter has founded upon it a method of analyzing mixtures of liquids.

This unchangeable number was termed the "specific refractive energy" of the substance, and it seemed to hold good notwithstanding a change from the solid to the liquid or the gaseous condition. It was early observed that the specific refractive energy of a compound bore a close resemblance to the mean of the specific refractive energies of its components. Landolt, by multiplying this number by the chemical equivalent, facilitated the calculation greatly. He termed this new number the "refraction-equivalent," $P^{\mu-1}_d$ and proofs have rapidly accumulated that the number is little affected, not only by temperature, change of aggregate condition, mixture, or solution, but even by strong chemical combination.

Thus diamond, which is crystallized carbon, has the refraction-equivalent 5.0; sulphur has 16.0. Bisulphide of carbon, $C S_2$, which is nearly the most refractive liquid known, should therefore be represented by $5 + 2 \times 16$, that is 37.0. The experimental number is 37.3. But the diamond will burn in oxygen, and is thus converted into carbonic anhydride, while it is possible to reduce this gas into another containing only half the amount of oxygen, namely, carbonic oxide. The refraction-equivalents of these gases, as deduced from Dulong's observations, are respectively 10.03 and 7.53; but the difference between $C O_2$ and $C O$ is one equivalent of oxygen, and the difference between the above numbers is 2.5. This then may be taken as the refraction-equivalent of oxygen, and subtracting it from $C O = 7.53$ we have remaining $C = 5.03$, practically the same number as that obtained directly from crystallized carbon. Similarly, but generally by more indirect methods, it has been determined that this element, whether

pure as diamond or combined with other elements to form gases as the above-mentioned, coal-gas, or cyanogen, or liquids as chloride of carbon, benzole, oil of turpentine, alcohol, or ether, or solids as paraffin, sugar, or camphor, is still exerting the same influence on the rays of light that set its particles in motion, an influence that we can express by the number 5.0. Again to revert to sulphur, the two salts sulpho-cyanide and cyanide of potassium—K S Cy and K Cy—differ by one equivalent of this element, and their refraction-equivalents as determined from their aqueous solutions are respectively 33.4 and 17.1, numbers differing by 16.3, a number almost identical with that reckoned from molten sulphur. In this way the refraction-equivalents of a large number of the elements have been determined; and the following table comprises what seem the most probable numbers among those that have been hitherto published by Landolt, Haagen, and Schrauf, as well as the speaker:—

	Atomic weight.			Refraction-equivalent.	
Hydrogen	1.0	..	1.3
Chlorine	35.5	..	9.8
Bromine	80.0	..	15.7
Iodine	127.0	..	24.4
Oxygen	16.0	..	3.0
Sulphur	32.0	..	16.0
Carbon	12.0	..	5.0
Silicium	28.0	..	6.2
Nitrogen	14.0	..	4.1
Phosphorus	31.0	..	18.5
Arsenic	75.0	..	16.0
Antimony	122.0	..	25.7
Vanadium	51.4	..	25.4
Sodium	23.0	..	4.9
Tin	118.0	..	19.2
Copper	63.4	..	11.2
Mercury	200.0	..	21.6

The above numbers are reckoned for the red ray. Most of them can as yet claim to be considered only as approximative; and it seems certain that some elements, as oxygen and sulphur, have more than one refraction-equivalent.

Vanadium, though included in the above table, has only just been determined, and that from the oxy-trichloride which Professor Roscoe exhibited a few weeks before. It is interesting, as it supports his theory of the close analogy of phosphorus and vanadium, for these two bodies, with sulphur, exceed all others in refraction and especially in dispersion.

The speaker stated that he was now engaged in examining the effect of salts in solution on the rays of light, and that he hoped to determine in this way the refraction-equivalents not only of a multitude of salts, but of the metallic elements themselves.

But the question may be asked, "If a substance has a refraction compounded of the refraction of its constituents, how can bodies such

as Iceland spar have two refractive indices?" Now these are crystalline bodies, or if uncrystallized they have become doubly refracting by being unequally heated or compressed. In either case we may suppose a different amount of tension in different directions; and the fact of the two rays being oppositely polarized points to some such difference of molecular arrangement. It is easy to understand that the change of tension or internal structure may act in the same way as a change of density in modifying the velocity of transmitted light, and therefore the amount of its refraction. But if we take the crystal to pieces by dissolving it, there can then no longer be unequal tension or unsymmetrical arrangement of particles, and it must have one refraction-equivalent. And this is always the case. The numbers deduced from Brewster's observations of the two rays of crystallized nitre are 16.3 and 25.0, while the equivalent of nitre dissolved in water is the intermediate number 21.8.

[J. H. G.]

Friday, May 8, 1868.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

C. GREVILLE WILLIAMS, Esq. F.R.S.

On the Artificial Formation of Organic Substances.

CHEMICAL researches are liable at various epochs to take special directions. Before 1830 organic chemistry was comparatively little studied. The simplification of the methods of organic analysis by Liebig took place at a most opportune moment, and gave an extraordinary impetus to the study of carbon compounds. So great was this influence that proximate and ultimate analysis made a progress the rapidity of which was unexampled in the history of science.

But chemists soon became dissatisfied with merely determining the composition of substances, and they very soon began eagerly to study their products of decomposition, and in this manner get a clue to the way in which nature had put them together.

The successful attack on this problem led to a much grander one suggesting itself. This was to utilize the insight analysis had given them into the constitution of substances, and to endeavour to build them up without the assistance of life. The speaker showed that we thus arrive at the two great engines of chemical research, *analysis* and *synthesis*.

He then proceeded to define and illustrate experimentally these terms.

In organic chemistry the information supplied by the analysis of a substance often renders its synthesis easy. Water was decomposed by a battery, and its properties and quantitative relations shown. The mixed gases were then introduced into a soap-bubble, so prepared as to last a considerable time. It was by a simple contrivance attached to a thread, and the lightness of the enclosed gases was shown by the fact that the bubble was able to raise the thread and a disc of paper into the air. The energy with which the mixed gases combine to form water was then shown by applying a light to the bubble, when it burst with a loud report. The *quantitative* synthesis of water was experimentally shown by passing hydrogen over cupric oxide in an apparatus which allowed of the collection of the water. It was then shown that in organic chemistry the molecules are generally too complex to be put together so easily; and this statement was proved by reference to the constitution of methylamine, the simplest of the organic alkaloids.

The speaker then went somewhat fully into the question of the propriety of the use of the terms "organic" and "inorganic." He showed also that all the attempts hitherto made at separating chemistry into two distinct branches had failed. Liebig's definition of organic chemistry as the "chemistry of compound radicles" being obviously inadequate, inasmuch as some compound radicles (such as sulphuryl and phosphoryl) are certainly inorganic.

Laurent's definition, "chemistry of carbon," is equally insufficient, inasmuch as carbonic anhydride and carbonic tetrachloride are as clearly inorganic as sulphuric anhydride or sodic chloride. He then proceeded to argue that chemistry was "one and indivisible," and stated that one of the chief aims of his discourse was to prove that assertion.

It was shown that until within the last few years all the specific attempts made to break the apparently natural barriers between organic and inorganic chemistry had proved failures.

It was true that in the course of the innumerable researches and experiments made by chemists, one or two of the simple organic bodies had presented themselves; but, like urea and cyanogen, they were substances which, as it were, hovered on the confines of inorganic chemistry, and would have been called inorganic had they not contained carbon.

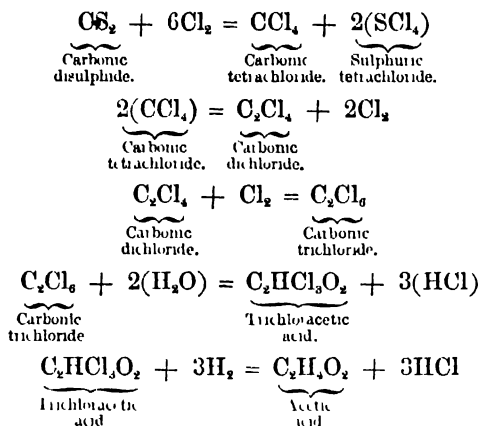
The grand problem, which consisted in taking the elements themselves, and building them up *gradatim* into the proximate principles existing in the tissues of plants and animals, until lately appeared almost hopeless. This apparent difficulty was shown to arise from the mistake of supposing the proximate principles of animals and vegetables to result from an occult power vaguely termed the "vital force." It was at one time supposed that the laws which regulate combination were either suspended or modified in the tissues of living creatures, but the speaker urged that whenever the proper reagents were made to act upon each other under the proper conditions, the same substances were produced which at one time were supposed to require the aid of vitality for their formation.

The problem of the "synthesis," or building up of the so-called organic substances, was then shown to present itself (in the present state of chemistry) under two aspects:—1st. Where they are prepared by the aid of reagents, which have themselves been produced directly or indirectly from animals or vegetables. 2nd. Where the synthesis was effected from the free elements themselves, from hydrogen and pure carbon.

The speaker then proceeded to enumerate some of the principal instances where substances originally derived from animals or vegetables had been formed synthetically. Wohler's synthesis of urea was shown to be one of the earliest in point of date, and his method was described, and also Kolbe's new process by the mere heating of ammoniac carbonate to a point just below that at which urea is decomposed.

One of the next most important steps in the history of synthesis was shown to be the conversion of carbonic disulphide into carbonic tetrachloride or perchlorinated marsh gas. Inasmuch as carbonic disulphide is a purely inorganic body, it is evident that any substance which can be formed from it is a case of true synthesis.

The following equations represent the steps by which acetic acid may be produced from carbonic disulphide :—



This important series of reactions, then, result in the production of acetic acid, one of the most marked of the so-called organic acids, from purely inorganic materials.

The synthesis of oxalic acid by the direct union of carbonic anhydride with sodium, as recently accomplished by Dr. Drechsel, was next described, and it was shown that as oxalic acid, by mere distillation, yields formic acid, the synthesis of the first acid leads directly to a new synthesis of the second.

The other modes of effecting the synthesis of formic acid were then pointed out, *viz.* :—Berthelot's process, which consists in heating potassic hydrate in an atmosphere of carbonic oxide; and Kolbe and Schmidt's method, by exposing potassium to a warm moist atmosphere of carbonic anhydride.

The speaker, in the course of his remarks on the constitution of formic acid, showed that the quantity of oxygen in it was so large that it only required one atom more to convert it into carbonic acid and water. Its easy oxidation was illustrated by letting it fall on plumbic dioxide in an apparatus which caused the evolved gas to pass into a solution of baric hydrate, the result being a copious precipitation of baric carbonate.

Having shown that acetic acid can be formed from carbonic disulphide and the chlorides of carbon, and oxalic and formic acids from the oxides of carbon, the speaker proceeded to indicate the modes

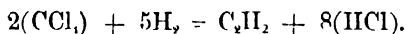
in which complex bodies, hitherto obtained from animal and vegetable sources, can be built up from elemental carbon and hydrogen.

If carbon can only be made to combine directly with hydrogen, no matter how simple the resulting compound may be, it becomes possible to effect the synthesis of a vast number of the most characteristic substances found in animals and vegetables.

This brilliant result has been accomplished through the agency of acetylene, a most remarkable hydrocarbon which was first noticed by Edmund Davy as long ago as 1836.

There are two methods by which acetylene can be formed from inorganic materials—one devised by Berthelot, and the other by the speaker. The first consists in passing a stream of hydrogen through a globe in which the voltaic arc (from 70 or 80 cells of a Grove's battery) is produced between carbon points. At this tremendous temperature the carbon unites directly with the hydrogen. The experiment was made, and the production of acetylene shown, by the formation of a precipitate in a solution of ammoniacal cuprous chloride.

The speaker then showed, experimentally, that much larger quantities of acetylene can be formed by the decomposition by the induction spark of carbonic tetrachloride in presence of hydrogen, in accordance with the equation:—



The experiment succeeded perfectly, and a large quantity of the cuprous acetylide was rapidly produced.

But the most simple and ready means of preparing acetylene was shown to be by drawing air through the flame of a common glass spirit-lamp, by means of an aspirator. So readily is the cuprous precipitate obtained by this means, that it suffices to draw a few cubic centimetres through the solution of ammoniacal cuprous chloride to obtain evidence of the presence of acetylene in the flame. The experiment was then made, and in a few seconds the solution became thick with the suspended precipitate.

The speaker had ascertained that all the homologues of olefiant gas give acetylene in abundance when subjected to the induction spark. Amylene does it readily in accordance with the annexed equation:—

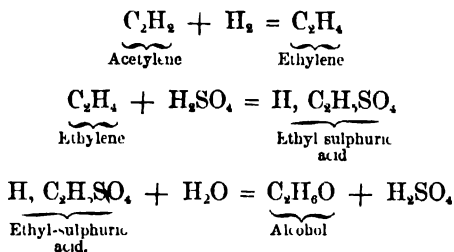


That the spark acted only in consequence of its high temperature, the speaker said, is rendered probable by the fact that if hydrogen be passed through carbonic tetrachloride, and then into a globe containing a platinum spiral, when the latter was heated to dull redness by three cells of a Grove's battery, no acetylene was produced; but when five cells were used, and the spiral became white hot, the cuprous

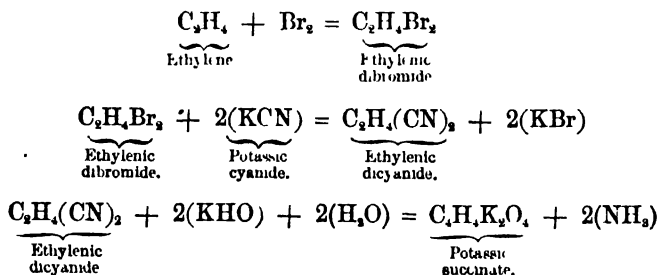
precipitate was obtained readily. The same result was stated to occur with anylene.

Simple as the formula of acetylene is, almost all the animal and vegetable substances which have been formed by pure synthesis may be obtained from it.

The following equations represent the steps by which alcohol may be "synthesised." It is proper to premise that the conversion of acetylene into olefiant gas is accomplished by treating the cuprous acetylides with zinc and ammonia, so as to obtain nascent hydrogen:—



The synthesis of succinic acid from acetylene was next shown in accordance with the annexed equations, omitting the synthesis of ethylene, which has been already given:—

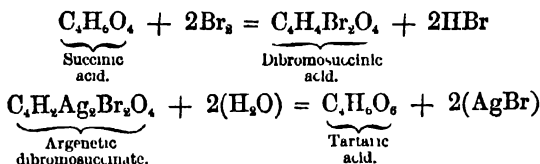


This mode of effecting the synthesis of succinic acid is due to the researches of Maxwell Simpson.

The beautiful appearance of succinic acid under the influence of polarized light was shown by the aid of the electric lamp. The specimen used had been artificially prepared.

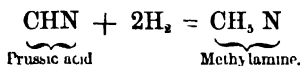
The speaker then proceeded to show that the synthesis of succinic acid was a direct step to that of tartaric acid. This latter reaction is due to the researches of Perkin and Duppa.

The artificial formation of succinic acid, starting with acetylene, having been proved, it is only necessary to start with that acid to prove the synthesis of tartaric acid from acetylene:—



The speaker next proceeded to show how the synthesis of the organic alkaloids could be effected from inorganic materials.

In the first place the fact that cyanides can be produced by heating carbon in presence of nitrogen and an alkali, is well known. The next step is to procure prussic acid by distilling cyanides with acids. From pure prussic acid methylamine, the simplest of the primary monamines, can easily be obtained, either by the aid of nascent hydrogen, or free hydrogen in the presence of spongy platinum.

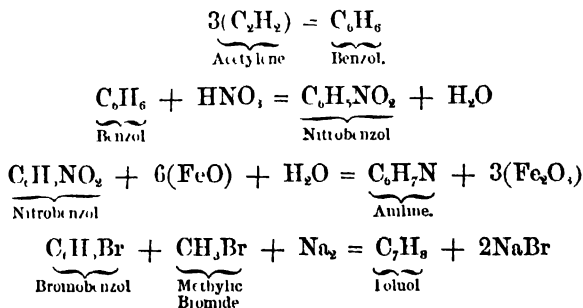


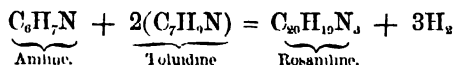
This equation has been realized by both the methods given above, the first by Mendius, the second by Debus.

It is also evident that as alcohol can be obtained from acetylene, that all the ethylic, primary, secondary, and tertiary monamines of Hofmann can now be synthetically formed. The steps being, (1) conversion of acetylene into olefiant gas; (2) passage of olefiant gas into alcohol; (3) alcohol into iodide of ethyl; (4) action of iodide of ethyl on ammonia.

Again, acetic acid, it has been shown, can be prepared from carbonic disulphide. Now acetic acid, by the action of a red heat, can be made to yield a number of the homologues of olefiant gas. The latter by treatment with excessively strong hydriodic acid, become converted into the iodides of the alcohol radicals (Berthelot). By following up this last reaction with pentylene, heptylene, octylene, and nonylene, the speaker succeeded in obtaining pentylamine, heptylamine, octylamine, and nonylamine.

The direct ascent from acetylene to the coal tar colours was then shown according to the following equations:—





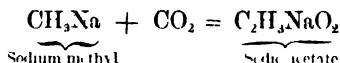
These transformations were all described at length. In effect acetylene passed through a red-hot tube becomes polymerized into benzol.

The passage of toluol into nitro-toluol and toluidine is omitted in the above equations, because the reactions are identical in kind with those of benzol into aniline.

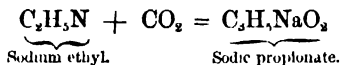
In describing benzol, experiments were shown illustrating the density of its vapour as compared with air. In one of these, benzol was poured into a large beaker containing a hot iron; at first the benzol assumed the spheroidal form, but, as the temperature fell, it became converted into vapour, which filled the beaker. A glass syphon was then introduced into the beaker, and the vapour drawn off as if it had been a liquid, and inflamed. The vapour descending through the syphon was then received into a warm beaker, from which it was decanted into another beaker in which it was inflamed.

The speaker then proceeded to show the way in which the synthesis of zinc ethyl could be effected; it is, however, unnecessary to follow the equations in detail, because, having already explained the manner in which alcohol can be synthesized from acetylene, it is obvious that zinc ethyl can be directly derived from that fluid.

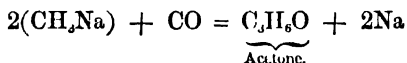
Wauklyn's interesting synthesis of acetic acid from sodium methyl was then shown to take place in accordance with the expression:



The method appears to be general, inasmuch as the same chemist has effected the synthesis of propionic acid:



And, substituting carbonic oxide for carbonic anhydride, we have—



The speaker stated that one of the most interesting of the cases of synthesis recently accomplished was that in which Mr. W. H. Perkin had succeeded in producing artificially the odoriferous principle of new hay and the tonquin bean.

The delicious fragrance of new hay is entirely due to the presence of the sweet-scented vernal grass, *anthoxanthum odoratum*. It is the same substance which is the cause of the sweet smell of the woodruff, *asperula odorata*; and the melilot, *melilotos officinalis*. It is also the flavouring ingredient in the *mai wein* of the Germans, which is perfumed with woodruff.

Until lately, nothing was known about coumarin, except that it was a colourless crystalline body, having the formula—



The crystals of coumarin appear very beautiful under the influence of polarized light. The image of some artificial coumarin, which had been fused and allowed to crystallize in a plate of glass, was then thrown upon the screen, and the light being polarized by the aid of Nicol's prisms, the crystals assumed the most gorgeous and varying colours as the prisms were rotated.

The clue to its constitution was shown to be the circumstance that when heated with potassic hydrate it yields salicylic and acetic acids. The production of salicylic acid from coumarin was then shown, experimentally, the presence of the acid being proved by its yielding a deep purple coloration with ferric chloride.

Artificial coumarin was obtained from the hydride of salicyl. By treatment with sodium it yielded hydride of sodium salicyl; this substance, heated with acetic anhydride, gave hydride of aceto-salicyl. This last substance was then distilled with acetic anhydride and sodic acetate, and when the temperature reached 290° , the distillate solidified to a mass of crystals of pure coumarin, having all the fragrance and beauty of that obtained from the tonquin bean.

The speaker then submitted that the assertion he had made at an early period of his discourse that there was no natural barrier between organic and inorganic chemistry, had been amply proved by the instances he had brought forward. He said that they had studied together that evening several cases where, starting from inorganic matter, they had ascended step by step until they had reached some, of the most complicated bodies secreted by animals and vegetables. What, he said, could be more distinctly inorganic than nitrogen, carbon, and oxygen? What more distinctly an animal secretion than urea? What more completely inorganic than acetylene? What more distinctly vegetable in origin than coumarin?

Chemists have then, so far, done what a very few years would have been regarded as possible only by aid of the vital force. A true organized substance, he said, is so definite that we can almost invariably determine its molecular weight, and it is generally crystalline. But when we come to the tissues we are dealing no longer with organic substances, but with organized beings, and we feel that we are approaching the barriers which separate the study of life from the study of matter. The bonds which unite them are so close that we cannot imagine life *without* matter, and it is equally difficult to conceive the assumption of vitality *by* matter; but we must never cease to look anxiously for the solution of the problem. The impossible is a horizon which recedes as we advance, and the *terra incognita* of to-day will to-morrow be boldly mapped upon every schoolboy's chart!

[C. G. W.]

Friday, May 22, 1868.

SIR HENRY HOLLAND, BART. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, M.B. F.R.S.

On some Effects of the Heat of the Oxy-hydrogen Flame.

I.

CHEMICAL changes, whether of combination or decomposition, result in the production of new bodies which, under the conditions of the change, have for the most part a greater stability than the original bodies.

One evidence of this greater stability is afforded by the development of a quantity of heat—the heat of chemical action—from the produced bodies having a smaller potential heat than the original ones.

It results, both from reason and experiment, that in order to undo or reverse any definite chemical action, just so much heat must be directly or indirectly expended as was evolved by the original action.

For the same quantity of heat evolved, the resulting temperature varies with the mass and kind of matter heated, and with the rapid or gradual evolution of the heat.

When the evolution of heat is instantaneous, the resulting temperature may be calculated from the quantity of heat evolved, and the mass and specific heat, &c., of the matter heated.

By a unit of heat is meant the quantity of heat necessary to raise the temperature of one kilogramme of water one degree centigrade, or more accurately from 0° to 1°.

II.

Every 18 grammes of water is a combination of two 1-gramme proportions of hydrogen H, with one 16-gramme proportion of oxygen O; and, by the combination of two grammes of hydrogen with sixteen grammes of oxygen, there are developed 68 units of heat.

Of these 68 units of heat, however, little more than 57 units are really due to the chemical action,—nearly 11 units of heat being evolved by the contraction of the original mixed gas into two-thirds its volume of steam, and by the further condensation of the resulting steam into 18 cubic centimetres of water.

While the quantity of heat evolved by the combination of a given quantity of oxygen and hydrogen is invariable, the intensity of the heat may vary from a scarcely recognisable rise of temperature up to the highest temperature of the oxy-hydrogen blowpipe flame, capable of fusing platinum and silica.

A most remarkable effect of the intense temperature resulting from the combination of oxygen and hydrogen into water, is the partial decomposition of water into oxygen and hydrogen, discovered by Mr. Grove in 1846.

At this high temperature, hydrochloric acid and carbonic anhydride gases also undergo partial decomposition, into hydrogen and chlorine, and into carbonous oxide and oxygen respectively.

Upon what do these singular decompositions by heat, of bodies formed with great evolution of heat, depend; or with what class of chemical phenomena may they be associated?

III.

Under certain familiar conditions, chemical action seemingly takes place to its utmost possible extent in a single direction only, with production of a maximum amount of the substance that is formed with maximum evolution of heat.

For example, taking atomic proportions in grammes, the heat of formation of chloride of zinc, ZnCl_2 , is 101 units, and the heat of formation of chloride of copper, CuCl_2 , is 60.5 units. Hence, with chlorine in solution and excess of both copper and zinc, there is finally produced the maximum possible amount of chloride of zinc and no chloride of copper.

Again, an addition of sufficient zinc to solution of chloride of copper, there is complete combination of chlorine with zinc and complete separation of chlorine from copper, *i. e.* complete burning of the one metal and complete unburning of the other.

IV.

But under simpler though less familiar conditions, chemical action habitually takes place in more than one direction simultaneously, with production of correlative products in varying proportions.

Thus, with hydrogen and excess of both chlorine and oxygen, although the heat of formation of oxide of hydrogen H_2O is 57 units, and the heat of formation of chloride of hydrogen 2HCl is only 47.5 units, yet, in this case, the hydrogen does not combine with the oxygen to the exclusion of the chlorine, but divides itself between the oxygen and the chlorine in proportions which vary with the conditions of the experiment.

In accordance with this result it is found that, at the same red heat, excess of chlorine will effect the partial decomposition of water with extrusion of oxygen; and, conversely, that excess of oxygen will effect the partial decomposition of hydrochloric acid with extrusion of chlorine.

So that, beginning with the two chemical substances, water and chlorine, or beginning with the two chemical substances, hydrochloric acid and oxygen, or beginning with the three chemical substances, hydrogen, chlorine, and oxygen, there exist, at a full red heat, the four chemical

substances, water, hydrochloric acid, chlorine, and oxygen; the proportions of the four substances depending certainly upon the relative quantities present of the elements concerned, and most probably also upon the temperature of the experiment.

Similarly, beginning with the one chemical substance, water (Grove), or beginning with the two chemical substances, oxygen and hydrogen (Bunsen), there always exist, at a sufficiently high temperature, the three chemical substances, water, oxygen, and hydrogen.

Although, by exposure to a red heat, the electrolytic mixture of oxygen and hydrogen gases becomes completely combined, or transformed into water, yet, as recently shown by Bunsen, at the high temperature of 2024 degrees, only one-half, and at the still higher temperature of 2844 degrees, only one-third of the mixture undergoes combination, the other one-half or two-thirds remaining in the state of mixed gas.

V.

Chemists are acquainted with many reciprocal actions comparable with those of chlorine upon water, and of oxygen upon hydrochloric acid, the most familiar instance being probably the decomposition of ignited oxide of iron by hydrogen with extrusion of iron, and the converse decomposition of oxide of hydrogen by ignited iron with extrusion of hydrogen.

Similarly, sodium will decompose the oxides of carbon, while carbon will decompose oxide of sodium; and just as a sufficient excess of chlorine may be made to effect the almost complete decomposition of a given quantity of water, so may a sufficient excess of carbon (or carbonous oxide) be made to effect the almost complete decomposition of a given quantity of sodium-oxide or zinc-oxide, as in the ordinary processes for obtaining the two metals; notwithstanding that, for an equal consumption of oxygen, the respective combination heats of sodium and zinc exceed by far the combination heat of carbon or carbonous oxide.

Again, although the combination heat of oxygen and carbonous oxide is 68 units, while that of oxygen and hydrogen is only 57 units, yet, as was shown by Bunsen many years ago, upon exploding a mixture of oxygen with a joint excess of carbonous oxide and hydrogen, the oxygen does not attach itself exclusively to the carbonous oxide, but divides itself between the carbonous oxide and hydrogen in a ratio determined by their relative proportions.

[W. O.]

Friday, June 12, 1868.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

EDWARD FRANKLAND, F.R.S.

PROFESSOR OF CHEMISTRY &c.

On the Source of Light in Luminous Flames.

THE most prolific source of error amongst mankind is the unquestioning acceptance of authoritative opinion. However much we may pride ourselves upon the sifting of the explanations of things by our own enlightened judgments, it cannot be denied that the *ipse dixit* mode of settlement is still wonderfully frequent amongst us. Not only is this the case with the public in general, but even the cultivators of science are not entirely innocent of the same weakness.

The essential difference between a fact and a theory is not always appreciated with sufficient vividness. The statement that "16 parts by weight of oxygen unite with 2 parts of hydrogen to form water," is considered by many, for instance, as perfectly synonymous with the assertion that "1 atom of oxygen unites with 2 atoms of hydrogen to form water."

The existence of an imponderable ethereal medium filling all space is often regarded as equally certain with the presence of a gaseous envelope surrounding our globe.

The atomic theory and the hypothesis of an ethereal medium are, at present, absolutely necessary, the one to the progress of chemistry, the other to the further development of physics; but neither this circumstance nor the splendid discoveries made by their aid can establish their truth. A mathematician starting from false data is sure to arrive at a false result; but it is far otherwise with theory, for false theories can, and constantly do, conduct to true facts. Thus Columbus's counterpoise theory of the earth led to the discovery of America, although that theory was nevertheless essentially false.

The most sober worker in science cannot progress without the assistance of theory to co-ordinate his facts, and to lead him on to further research. It is here that even a false theory is invaluable, and it is only when the theory continues to be held after it has become opposed to facts, that it exercises a prejudicial influence upon the progress of science. Then it hinders rather than expedites

the advance of the experimenter, and ought to be at once abandoned.

In pursuing the investigation forming the subject of this discourse, the speaker had been compelled thus to abandon a theory of the source of light in luminous flames, which he, in common with others, had derived from Davy's classical researches on flame.

Our text-books answer the question, *What is the source of light in a luminous gas or candle flame?* in the most positive and unanimous manner.

Selecting from some of the most celebrated, the following quotations may be made:—

"All our artificial lights depend upon the ignition of solid matter, in the intense heat developed by the chemical changes attendant on combustion."—*W. A. Miller*.

"Whenever hydrocarbons are imperfectly burnt, there is a deposition of carbon, and this temporary deposition of carbon is an *essential* condition for the production of the white light required in an ordinary flame."—*Williamson*.

"The illuminating power of the gas flame is therefore due to these *carbon particles*, which are afterwards burned nearer the border of the flame."—*Balfour Stewart*.

"The brightness or illuminating power of flame depends not only on the degree of heat, but likewise on the presence or absence of solid particles which may act as radiant points. A flame containing no such particles emits but a feeble light, even if its temperature is the highest possible."—*Watts*.

The speaker then proceeded to investigate a number of different flames: he showed that there are many flames possessing a high degree of luminosity, which cannot possibly contain solid particles. Thus the flame of metallic arsenic burning in oxygen emits a remarkably intense white light; and as metallic arsenic volatilizes at 180° C., and its product of combustion, arsenious anhydride, at 218° C., whilst the temperature of incandescence in solids is at least 500° C., it is obviously impossible here to assume the presence of ignited solid particles in the flame. Again, if carbonic disulphide vapour be made to burn in oxygen, or oxygen in carbonic disulphide vapour, an almost insupportably brilliant light is the result; now fuliginous matter is never present in any part of this flame, and the boiling point of sulphur (440° C.) is below the temperature of incandescence, so that the assumption of solid particles in the flame is here also inadmissible. If the last experiment be varied by the substitution of nitric oxide gas for oxygen, the result is still the same; and the dazzling light produced by the combustion of these compounds is also so rich in the more refrangible rays, that it has been employed in taking instantaneous photographs, and for exhibiting the phenomena of fluorescence. Lastly, amongst the chemical reactions celebrated for the production of dazzling light, there are few which surpass the active combustion of phosphorus in oxygen. Now phosphoric anhydride, the product of

this combustion, is volatile at a red heat,* and it is therefore manifestly impossible that this substance should exist in the solid form at the temperature of the phosphorus flame, which far transcends the melting point of platinum.

For these reasons, and for others which the speaker had stated in a course of lectures on Coal-Gas, delivered in March, 1867, and printed in the 'Journal of Gas Lighting,' he considered that incandescent particles of carbon are not the source of light in gas and candle flames, but that the luminosity of these flames is due to radiations from dense, but transparent hydrocarbon vapours. As a further generalization from the above-mentioned experiments, he was led to the conclusion that dense gases and vapours become luminous at much lower temperatures than aeriform fluids of comparatively low specific gravity; and that this result is to a great extent, if not altogether, independent of the nature of the gas or vapour, inasmuch as he found that gases of low density, which are not luminous at a given temperature when burnt under common atmospheric pressure, become so when they are simultaneously compressed. Thus mixtures of hydrogen and carbonic oxide with oxygen emit but little light when they are burnt or exploded in free air; but exhibit intense luminosity when exploded in closed glass vessels, so as to prevent their expansion at the moment of combustion.

In a communication just made to the Royal Society the speaker had described the extension of these experiments to the combustion of jets of hydrogen and carbonic oxide in oxygen under a pressure gradually increasing to twenty atmospheres. Those experiments, which were conducted in the laboratory of the Royal Institution, were made in a strong wrought-iron vessel furnished with a thick glass plate of sufficient size to permit of the optical examination of the flame. The appearance of a jet of hydrogen burning in oxygen under the ordinary atmospheric pressure was exhibited. On increasing the pressure to two atmospheres, the previously feeble luminosity was shown to be very markedly augmented, whilst at ten atmospheres' pressure, the light emitted by a jet about one inch long was amply sufficient to enable the observer to read a newspaper at a distance of two feet from the flame, and this without any reflecting surface behind the flame. Examined by the spectroscope, *the spectrum of this flame is bright and perfectly continuous from red to violet.*

With a higher initial luminosity, the flame of carbonic oxide in oxygen becomes much more luminous at a pressure of ten atmospheres than a flame of hydrogen of the same size and burning under the same pressure. The spectrum of carbonic oxide burning in oxygen under

* Davy mentions this fact in connection with his view of the source of luminosity in flames, and endeavours to explain the, to him, anomalous phenomenon. He says:—"Since this paper has been written, I have found that phosphoric acid volatilizes slowly at a strong red heat, but under moderate pressure it bears a white heat; and in a flame so intense as that of phosphorus, the elastic force must produce the effect of compression."—*Davy's Works*, vol. vi., p. 48.

a pressure of fourteen atmospheres is very brilliant and perfectly continuous.

If it be true that dense gases omit more light than rare ones when ignited, the passage of the electric spark through different gases ought to produce an amount of light varying with the density of the gas; and the speaker showed that electric sparks passed as nearly as possible, under similar conditions, through hydrogen, oxygen, chlorine, and sulphurous anhydride, emit light, the intensity of which is very slight in the case of hydrogen, considerable in that of oxygen, and very great in the case of chlorine and sulphurous anhydride. On passing a stream of induction sparks through the gas standing over liquefied sulphurous anhydride in a strong tube at the ordinary temperature, when a pressure of about three atmospheres was exerted by the gas, a very brilliant light was obtained. A stream of induction sparks was passed through air confined in a glass tube connected with a condensing syringe, and the pressure of the air being then augmented to two or three atmospheres, a very marked increase in the luminosity of the sparks was observed, whilst on allowing the condensed air to escape, the same phenomena were observed in the reverse order.

Way's mercurial light was also exhibited as an instance of intense light produced by the ignition of the heavy vapour of mercury.

The gases and vapours just mentioned have the following relative densities:—

Hydrogen	1
Air	11.5
Oxygen	16
Sulphurous anhydride	32
Chlorine	35.5
Mercury	100
Phosphoric anhydride	71 or 112

The feeble light emitted by phosphorus when burning in chlorine seems, at first sight, to be an exception to the law just indicated, for the density of the product of combustion (phosphorous trichloride) 68.7 would lead us to anticipate the evolution of considerable light. But it must be borne in mind that the luminosity of a flame depends also upon its temperature, and it can be shown that the temperature in this case is probably greatly inferior to that produced by the combustion of phosphorus in oxygen. We have not all the necessary data for calculating the temperature of these flames, but, according to Andrews, phosphorus burnt in oxygen gives 5747 heat units, which, divided by the weight of the product from one grain of phosphorus, gives 2500 units. When phosphorus burns in chlorine, it gives only, according to the same authority, 2085 heat units, which, divided as before by the weight of the product, gives 470 units. It is therefore evident that the temperature in the latter case must be greatly below that produced in the former, unless the specific heat of phosphoric anhydride be enormously higher than that of phosphorous trichloride. The speaker had, in fact, found that if the temperature of the flame of phosphorus, burning in chlorine, be raised about 500° C. by previously

heating both elements to that extent, the flame emitted a brilliant white light.

To return to ordinary luminous flames, the argument of the *necessity* of solid particles to explain their luminosity obviously falls to the ground; and a closer examination into the evidence of the existence of these particles reveals its extreme weakness. Soot from a gas flame is not elementary carbon, it always contains hydrogen. The perfect transparency of the luminous portion of flame also tends to negative the idea of the presence in it of solid particles. The continuous spectrum of gas and candle flames does not require, as is commonly supposed, the assumption of solid particles. The spectra of the flames of carbonic oxide in air, of carbonic disulphide, arsenic, and phosphorus in oxygen, are continuous, and so, as we have seen, is that of hydrogen burning in oxygen under a pressure of ten atmospheres. It is to the behaviour of hydrocarbons under the influence of heat that we must look for the source of luminosity in a gas flame. These gradually lose hydrogen, whilst their carbon atoms coalesce to form compounds of greater complexity, and consequently of greater vapour density. Thus marsh-gas ($C H_4$) becomes acetylene ($C_2 H_2$), and the density increases from 8 to 13. Again, olefiant gas ($C_2 H_4$) forms naphthaline ($C_{10} H_8$), when the vapour density augments from 14 to 64. These are some of the dense hydrocarbons which are known to exist in a gas flame, but there are doubtless others still more dense; pitch, for instance, must consist of the condensed vapours of such heavy hydrocarbons, for it distils over from the retorts in the process of gas-making. Candle flames are similarly constituted. The direct dependence of the luminosity of gas and candle flames upon atmospheric pressure, also strongly confirms the view that the light of these flames is due to incandescent dense vapours.

This inquiry cannot be confined to terrestrial objects. Science seeks alike for law in the meanest and grandest objects of creation. From questioning a candle she addresses herself to suns, stars, nebulae, and comets; the same considerations which have just been applied to gas and candle flames are equally pertinent to these great cosmical sources of light.

[E. F.]

Friday, January 15, 1869.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

PROFESSOR TYNDALL, LL.D. F.R.S.

On Chemical Rays, and the Light of the Sky.

THE first physical investigation of any importance in which, jointly with my friend Professor Knoblauch, I took part, bore the title, "The Magneto-optic Properties of Crystals, and the Relation of Magnetism and Diamagnetism to Molecular Arrangement."* This investigation compelled me to reflect upon the structure of crystals, on their optical properties in relation to that structure, and more particularly on the striking phenomena exhibited by many of them in the field of a sufficiently powerful magnet. These were evidently due to the manner in which the molecules of the crystals were built together by the force of crystallization: and it was natural, if not necessary for me, to employ such strength of imagination as I possessed in obtaining a mental picture of this molecular architecture. The inquiry gave a tinge and bias to my subsequent scientific thought, rendering, as it did, the conceptions and pursuit of molecular physics pleasant to me. Its influence is to be traced in most of my scientific work. The first Lecture, for example, which I ever delivered in this theatre, was "On the Influence of Material Aggregation on the Manifestations of Force;" by "material aggregation" being meant the way in which, by nature or by art, the particles of matter are arranged together. In 1853 I also published a paper "On Molecular Influences," in which common heat was made the explorer of organic structure. In the "Bakerian Lecture," given before the Royal Society in 1855, the same idea and phraseology crop out. The Bakerian Lecture for 1864 bears the title "Contributions to Molecular Physics." And all through the investigations which have occupied me during the last ten years, my wish and aim have been to make radiant heat an instrument by which to lay hold of the ultimate particles of matter.

The labours now to be considered lie in the same direction. In the researches just referred to, I employed tubes of glass and brass, called, for the sake of distinction, "experimental tubes," in which radiant heat was acted upon by the gases and vapours subjected to examination. Wishing, two or three months ago, to render visible what occurred within these tubes on the entrance of the gases or

* 'Philosophical Magazine,' July, 1850.

vapours, I found it necessary to intensely illuminate their interiors. The source of illumination chosen was the electric light; the beam of which, converged by a suitable lens, was sent along the axis of the tube. The dirt and filth in which we habitually live were strikingly revealed by this method of illumination. For, wash our tube as we might with water, alcohol, acid, or alkali, until its appearance in ordinary daylight was that of absolute purity, the delusive character of this appearance was in most cases revealed by the electric beam. In fact, in air so dirty as that which supplies our lungs—and I will not say that we could get on healthily without the “dirt”^{*}—it is not possible to be more than approximately cleanly.

Vapours of various kinds were sent into a glass experimental tube a yard in length, and about three inches in diameter. As a general rule, the vapours were perfectly transparent; the tube when they were present appearing as empty as when they were absent. In two or three cases, however, a faint cloudiness showed itself within the tube. This caused me a momentary anxiety, for I did not know how far, in describing my previous experiments, actions might have been ascribed to pure cloudless vapour which were really due to those newly-observed *nebulae*. Intermittent discomfort, however, is the normal feeling of the investigator; for it drives him to closer scrutiny, to greater accuracy, and often, as a consequence, to new discovery. It was soon found that the *nebulae* revealed by the beam were also generated by the beam, and the observation opened a new door into that region inaccessible to sense, which embraces so much of the intellectual life of the physical investigator.

What are those vapours of which we have been speaking? They are aggregates of *molecules*, or small masses of matter, and every molecule is itself an aggregate of smaller parts called *atoms*. A molecule of aqueous vapour, for example, consists of two atoms of hydrogen and one of oxygen. A molecule of ammonia consists of three atoms of hydrogen and one of nitrogen, and so of other substances. Thus the molecules themselves inconceivably small, are made up of distinct parts still smaller. When, therefore, a compound vapour is spoken of, the corresponding mental image is an aggregate of molecules separated from each other, though still exceedingly near, each of these being composed of a group of atoms still nearer to each other. So much for the *matter* which enters into our conception of a vapour.[†] To this must now be added the idea of *motion*. The molecules have motions of their own as *wholes*; their constituent atoms have also motions of

^{*} This “dirt” consists in great part of organic germs, of the functions of which in the animal economy we are as yet ignorant.

[†] Newton seemed to consider that the molecules might be rendered visible by microscopes; but of the atoms he appears to have entertained a different opinion. He finely remarks:—“It seems impossible to see the more secret and noble works of nature within the corpuscles, by reason of their transparency.” (Herschel, “On Light,” Art. 1145.)

their own, which are executed independently of those of the molecules; just as the various movements on the earth's surface are executed independently of the orbital revolution of our planet.

The vapour molecules are kept asunder by forces which, virtually or actually, are forces of repulsion. Between these elastic forces and the atmospheric pressure under which the vapour exists, equilibrium is established as soon as the proper distances between the molecules have been assumed. If, after this, the molecules be urged nearer to each other by a momentary force, they recoil as soon as the force is expended. If by the exercise of a similar force they be separated more widely, when the force ceases to act they again approach each other. The case is different as regards the constituent atoms.

And here let me remark that we are now upon the very outmost verge of molecular physics; and that I am attempting to familiarize your minds with conceptions which have not yet obtained universal currency even among chemists; which many chemists, moreover, might deem untenable. But, tenable or untenable, it is of the highest scientific importance to discuss them. Let us, then, look mentally at our atoms grouped together to form a molecule. Every atom is held apart from its neighbours by a force of repulsion; why, then, do not the mutually repellent members of this group part company? The molecules *do* separate from each other when the external pressure is lessened or removed, but the atoms do not. The reason of this stability is that *two* forces, the one attractive and the other repulsive, are in operation between every two atoms; and the position of every atom—its distance from its fellows—is determined by the equilibration of these two forces. If the atoms come too near, repulsion predominates and drives them apart; if too distant, attraction predominates and draws them together. The point at which attraction and repulsion are equal to each other is the atom's *position of equilibrium*. If not absolutely cold—and there is no such thing as absolute coldness in our corner of nature—the atoms are always in a state of vibration, their vibrations being executed to and fro *across their positions of equilibrium*.

Into a vapour thus constituted, we have now to pour a beam of light. But what, in the first instance, *is* a beam of light? It is a train of innumerable waves, excited in, and propagated through, an almost infinitely attenuated and elastic medium, which fills all space, and which we name the *Æther*. These waves of light are not all of the same size: some of them are much longer and higher than others. Now the short waves and the long ones move with the same rapidity through space, just as short and long waves of sound travel with the same rapidity through air. Hence the shorter waves must follow each other in quicker succession than the longer ones. The different rapidities with which the waves of light impinge upon the retina, or optic nerve, give rise in consciousness to differences of *colour*. There are however, numberless waves emitted by the sun and other luminous bodies which reach the retina, but which are incompetent to excite the

sensation of light. If the lengths of the waves exceed a certain limit, or if they fall short of a certain other limit, they cannot generate vision. And it is to be particularly borne in mind that the capacity to produce *light* does not depend so much on the *strength* of the waves, as on their *periods of recurrence*. I have often permitted waves to enter my own eye, of a power which, if differently distributed, would have instantly and utterly ruined the optic nerve, but which failed to produce any impression whatever upon consciousness, because their periods were not those demanded by the retina.

The elements of all the conceptions with which we shall have subsequently to deal are now in your possession. And you will observe that though we are speaking of things which lie entirely beyond the range of the senses, the conceptions are as truly *mechanical* as they would be if we were dealing with ordinary masses of matter, and with waves of sensible magnitude. I do not think that any really scientific mind at the present day will be disposed to draw a substantial distinction between chemical and mechanical phenomena. They differ from each other as regards the magnitude of the masses involved; but in this sense the phenomena of astronomy differ, also, from those of ordinary mechanics. The main bent of the natural philosophy of a future age will probably be to chasten into order, by subjecting it to mechanical laws, the existing chaos of chemical phenomena.

Whether we see rightly or wrongly—whether our intellection be real or imaginary—it is of the utmost importance in science to aim at perfect clearness in the description of all that comes, or seems to come, within the range of the intellect. For if we are right, clearness of utterance forwards the cause of right; while if we are wrong, it ensures the speedy correction of error. In this spirit, and with the determination at all events to speak plainly, let us deal with our conceptions of æther waves and molecules. Supposing a wave, or a train of waves, to impinge upon a molecule so as to urge all its parts with the same motion, the molecule would move bodily as a whole, but because they are animated by a *common motion* there would be no tendency of its constituent atoms to separate from each other. *Differential motions* among the atoms themselves would be necessary to effect a separation, and if such motions be not introduced by the shock of the waves, there is no mechanical ground for the decomposition of the molecule.

It is, however, difficult to conceive the shock of a wave, or a train of waves, so distributed among the atoms as to cause no strain amongst them. For atoms are of different weights, probably of different sizes; at all events it is almost certain that the ratio of the mass of the atom to the surface it presents to the action of the waves is different in different cases. If this be so, and I think the probabilities are immensely in favour of its being so, then every wave which passes over a molecule tends to decompose it—tends to carry away from their weightier and more sluggish companions those atoms which, in relation to their mass, present the largest resisting surfaces to the

motion of the waves. The case may be illustrated by reference to a man standing on the deck of a ship. As long as both of them share equally the motions of the wind or of the sea, there is no tendency to separation. In chemical language, they are in a state of combination. But a wave passing over it finds the ship less rapid in yielding to its motion than the man; the man is consequently carried away, and we have what may be regarded as decomposition.

Thus the conception of the decomposition of compound molecules by the waves of æther comes to us recommended by *a priori* probability. But a closer examination of the question compels us to supplement, if not materially to qualify, this conception. It is a most remarkable fact, that the waves which have thus far been found most effectual in shaking asunder the atoms of compound molecules are those of least mechanical power. *Billows*, to use a strong comparison, are incompetent to produce effects which are readily produced by *ripples*. It is, for example, the violet and ultra-violet rays of the sun that are most effectual in producing these chemical decompositions; and, compared with the red and ultra-red solar rays, the energy of these "chemical rays" is infinitesimal. This energy would probably in some cases have to be multiplied by millions to bring it up to that of the ultra-red rays; and still the latter are powerless where the smaller waves are potent. We here observe a remarkable similarity between the behaviour of chemical molecules and that of the human retina. The energy transmitted to the eye from a candle-flame half-a-mile distant is more than sufficient to inform consciousness; while waves of a different period, possessing twenty thousand million times this energy, have been suffered to impinge upon my own retina, with an absolute unconsciousness of any effect whatever—mechanical, physiological, chemical, or thermal.

Whence, then, the power of these smaller waves to unlock the bonds of chemical union? If it be not a result of their strength, it must be, as in the case of vision, a result of their periods of recurrence. But how are we to figure this action? I should say thus: the shock of a single wave produces no more than an infinitesimal effect upon an atom or a molecule. To produce a larger effect, the motion must *accumulate*, and for wave-impulses to accumulate, they must arrive in periods identical with the periods of vibration of the atoms on which they impinge. In this case each successive wave finds the atom in a position which enables that wave to add its shock to the sum of the shocks of its predecessors. The effect is mechanically the same as that due to the timed impulses of a boy upon a swing. The single tick of a clock has no appreciable effect upon the unvibrating and equally long pendulum of a distant clock; but a succession of ticks, each of which adds, at the proper moment, its infinitesimal push to the sum of the pushes preceding it, will, as a matter of fact, set the second clock going. So likewise a single puff of air against the prong of a heavy tuning-fork produces no sensible motion, and, consequently, no audible sound; but a succession of puffs, which follow each other

in periods identical with the tuning-fork's period of vibration, will render the fork sonorous. I think the chemical action of light is to be regarded in this way. Fact and reason point to the conclusion that it is the heaping up of motion on the atoms, in consequence of their synchronism with the shorter waves, that causes them to part company. This I take to be the mechanical cause of these decompositions which are effected by the waves of æther.

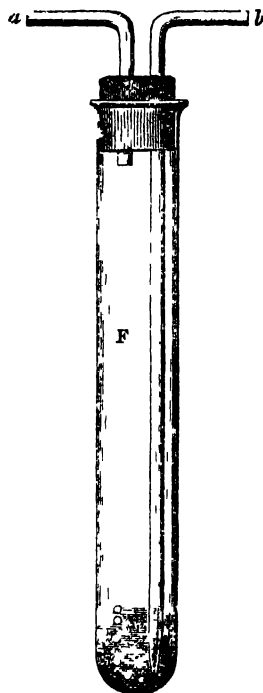
And now let us return to that faint cloudiness, already mentioned, from which, as from a germ, these considerations and speculations have sprung. It has been long known that light effected the decomposition of a certain number of bodies. The transparent iodide of ethyl, or of methyl, for example, becomes brown and opaque on exposure to light, through the discharge of its iodine. The art of photography is founded on the chemical actions of light; so that it is well known that the effects for which the foregoing theoretic considerations would have prepared us, are not only probable, but actual.

But the method employed in the experiments in which the cloudiness above referred to was observed, and which consists simply in offering the vapours of volatile substances to the action of light, enables us not only to give such experiments a beautiful form, but also to give a vast extension to the operations of light, or rather of radiant force, as a chemical agent. It also enables us to illustrate in our laboratories actions which have been hitherto performed only in the laboratory of nature. A few of these actions of a representative character I have now to bring before you; and, in doing so, I will take advantage of the fact that, in a great number of cases, one or more of the substances into which the waves of light break up compound molecules are comparatively *involatile*. These products of decomposition require a greater heat than is required by the vapours from which they are derived to keep them in the gaseous form; and hence, if the space in which these new bodies are liberated be of the proper temperature, they will not remain in the vaporous condition, but will precipitate themselves as liquid particles, thus forming visible clouds upon the beam to the action of which they owe their existence.

We will now commence our illustrative experiments. I hold in my hand a little flask, F, which is stopped by a cork, pierced in two places. Through one orifice passes a narrow glass tube, *a*, which terminates immediately under the cork; through the other orifice passes a similar tube, *b*, descending to the bottom of the little flask, which is filled to a height of about an inch with a transparent liquid. The name of this liquid is *nitrate of amyl*, in every molecule of which we have 5 atoms of carbon, 11 of hydrogen, 1 of nitrogen, and 2 of oxygen. Upon this group the waves of our electric light will be immediately let loose. The large horizontal tube that you see before you is what I have called an "experimental tube;" it is connected with our small flask, a stop-cock, however, intervening between them, by means of which the passage between the flask and the

experimental tube can be opened or closed at pleasure. The other tube, passing through the cork of the flask and descending into the liquid, is connected with a U-shaped vessel, filled with fragments of clean glass, covered with sulphuric acid. In front of the U-shaped vessel is a narrow tube stuffed with cotton-wool. At one end of the experimental tube is our electric lamp; and here, finally, is an air-pump, by means of which the tube has been exhausted. We are now ready for experiment.

Opening the cock cautiously, the air of the room passes, in the first place, through the cotton-wool, which holds back the numberless organic germs and inorganic dust-particles floating in the atmosphere. The air, thus cleansed, passes into the U-shaped vessel, where it is *dried* by the sulphuric acid. It then descends through the narrow tube to the bottom of the little flask, and escapes there through a small orifice into the liquid. Through this it bubbles, loading itself to some extent with the nitrite of amyl vapour, and then the air and vapour enter the experimental tube together.



The closest scrutiny would now fail to discover anything within this tube; it is, to all appearance, absolutely empty. The air and the vapour are both invisible. We will permit the electric beam to play upon this vapour. The lens of the lamp is so situated as to render the beam slightly convergent, the focus being formed in the vapour at about the middle of the tube. You will notice that the tube remains dark for a moment after the turning on of the beam; but the chemical action will be so rapid that attention is requisite to mark this interval of darkness. I ignite the lamp; the tube for a moment seems empty; but suddenly the beam darts through a luminous white cloud, which has banished the preceding darkness. It has, in fact, shaken asunder the molecules of the nitrite of amyl, and brought down upon itself a shower of liquid particles which cause it to flash forth in your presence like a solid luminous spear. It is worth while to mark how this experiment illustrates the fact, that however intense a luminous beam may be, it remains invisible unless it has something to shine upon. *Space*, though traversed by the rays from all suns and all stars, is itself unseen. Not even the æther which fills space, and whose motions are the light of the universe, is itself visible.

You notice that the end of the experimental tube most distant from the lamp is free from cloud. Now the nitrite of amyl vapour is there also, but it is unaffected by the powerful beam passing through it. Let us make the transmitted beam more concentrated by receiving it on a concave silver mirror, and causing it to return by reflection into the tube. It is still powerless. Though a cone of light of extraordinary intensity now traverses the vapour, no precipitation occurs, no trace of cloud is formed. Why? Because the very small portion of the beam competent to decompose the vapour is quite exhausted by its work in the frontal portions of the tube. The great body of the light which remains, after this sifting out of the few effectual rays, has no power over the molecules of nitrite of amyl. We have here, strikingly illustrated, what has been already stated regarding the influence of *period*, as contrasted with that of *strength*. For the portion of the beam which is here ineffectual has probably more than a million times the absolute energy of the effectual portion. It is energy specially related to the atoms that we here need, which specially related energy being possessed by the feeble waves, invests them with their extraordinary power. When the experimental tube is reversed so as to bring the undecomposed vapours under the action of the *unsifted* beam, you have instantly this fine luminous cloud precipitated.

The light of the sun also effects the decomposition of the nitrite of amyl vapour. A small room in the Royal Institution, into which the sun shone, was partially darkened, the light being permitted to enter through an open portion of the window-shutter. In the track of the beam was placed a large plano-convex lens, which formed a fine convergent cone in the dust of the room behind it. The experimental tube was filled in the laboratory, covered with a black cloth, and carried into the partially darkened room. On thrusting one end of the tube into the cone of rays behind the lens, precipitation within the cone was copious and immediate. The vapour at the distant end of the tube was shielded by that in front; but on reversing the tube, a second and similar splendid cone was precipitated.

Now let us pause for a moment and glance at the ground over which we have passed. We have defined a vapour as an aggregate of molecules mutually repellent, but hindered from indefinitely retreating from each other by an external pressure. We have defined a molecule as an aggregate of atoms maintained in positions of equilibrium by the equalized action of two opposing forces, and always oscillating to and fro across those positions. We have defined a beam of light as a train of innumerable waves, and have illustrated their chemical action. We have learned that it is not the magnitude or power of the waves, so much as their periods of recurrence, that renders them effectual as chemical agents. We have also seen how the luminous beam is sifted by the vapour which it decomposes, and deprived of those rays which are competent to effect the decomposition. The effects, moreover, obtained with the electric beam are also produced by the beams of the sun.

And here I would ask you to make familiar to your minds the idea that no chemical action can be produced by a ray that does not involve the destruction of the ray. But the term "ray" is unsatisfactory to us at present, when our desire is to abolish all vagueness, and to affix a definite physical significance to each of our terms. Abandoning the term ray as loose and indefinite, we have to fix our thoughts upon the *waves* of light; and to render clear to our minds that those waves which produce chemical action do so by delivering up their own motion to the molecules which they decompose. We have here forestalled to some extent a question of great importance in molecular physics, which, however, is worthy of being fixed more definitely in your mind; it is this: When the waves of ether are intercepted by a compound vapour, is the motion of the waves transferred to the molecules of the vapour, or to the atoms of the molecules? We have thus far leaned to the conclusion that the motion is communicated to the atoms; for if not to these individually, why should they be shaken asunder? The question, however, is capable of, and is worthy of, another test, the bearing and significance of which you will immediately appreciate.

As already explained, the molecules are held in their positions of equilibrium by their mutual repulsion on the one side, and by an external pressure on the other. Their rate of vibration, if they vibrate at all, must depend upon the elastic force which they mutually exert. If this force be changed, the rate of vibration must change along with it; and after the change the molecules could no longer absorb the waves which they absorbed prior to the change. Now the elastic force between molecule and molecule is utterly altered when a vapour passes to the liquid state. Hence, if the liquid absorbs waves of the same period as its vapour, it is a proof that the absorption is not effected by the molecules. Let us be perfectly clear on this important point. Those waves are absorbed whose vibrations synchronize with those of the molecules or atoms on which they impinge; a principle which is sometimes expressed by saying that bodies radiate and absorb the same rays. This great law, as you know, is the foundation of spectrum-analysis; it enabled Kirchhoff to explain the lines of Fraunhofer, and to determine the chemical composition of the atmosphere of the sun. If then, after such a change as that involved in the passage of a vapour to the liquid state, the same waves are absorbed as were absorbed prior to the passage, it is a proof that the molecules, which must have utterly changed *their* periods, cannot be the seat of the absorption; and we are driven to conclude that it is to the *atoms*, whose rates of vibration are unchanged by the change of aggregation, that the wave-motion is transferred. If experiment should prove this identity of action on the part of a vapour and its liquid, it would establish in a new and striking manner the conclusion to which we have previously leaned.

We will now resort to the experimental test. In front of this experimental tube, which contains a quantity of the nitrite of amyl

vapour, is placed a glass cell a quarter of an inch in thickness, filled with the liquid nitrite of amyl. I send the electric beam first through the liquid and then through its vapour. The luminous power of this beam is very great but it can make no impression upon the vapour. The liquid has robbed it completely of its effective waves. I remove the liquid ; chemical action immediately commences, and in a moment we have the apparently empty tube filled with this bright cloud, precipitated by one portion of the beam, and illuminated by another. I re-introduce the liquid : the chemical action instantly ceases. I again remove the liquid, and the action commences once more. Thus we uncover in part the secrets of this world of molecules and atoms.

Instead of employing air as the vehicle by which the vapour is carried into the experimental tube, we may employ oxygen, hydrogen, or nitrogen. With hydrogen curious effects are observed, due to the sinking of the clouds through the extremely light gas in which they float. They illustrate, without proving, the argument of those who say that the clouds of our own atmosphere could not float if the cloud particles were not little bladders, instead of full spheres. Before you is a tube filled with the nitrite of amyl vapour, which has been carried into the tube by hydrogen gas. On sending the beam through the tube a delicate bluish-white cloud is precipitated. A few strokes of the pump clear the tube of this cloud, but leave a residue of vapour behind. Again turning in the beam we have a second cloud, more delicate than the first, precipitated. This may be done half-a-dozen times in succession. A residue of vapour will still linger in the tube sufficient to yield a cloud of exquisite delicacy, both as regards colour and texture.

Besides the nitrite of amyl a great number of other substances might be employed, which, like the nitrite, have been hitherto not known to be chemically susceptible to light. But I confine myself at present to this representative case. One point, however, in addition I wish to illustrate, chiefly because the effect is the same in kind as one of great importance in nature. In our atmosphere you know floats carbonic acid gas, which furnishes food to the vegetable world. But this food could not be consumed by plants and vegetables without the intervention of the sun's rays. And yet, as far as we know, these rays are powerless upon the free carbonic acid of our atmosphere. The sun can only decompose the gas when it is drunk in by the leaves of plants. In the leaves it is in close proximity with substances ready to take advantage of the loosening of the molecules of the carbonic acid by the waves of light. Incipient disunion being introduced by the solar rays, the carbon of the gas is seized upon by the leaf and appropriated, while the oxygen is discharged into the atmosphere.

The experimental tube now before you contains a quantity of a different vapour from that which we have hitherto employed. The liquid from which this vapour is derived is called the nitrite of butyl. On sending the electric beam through the vapour, which has been carried in by air, the chemical action is scarcely sensible. I add to

the vapour a quantity of air which has been permitted to bubble through hydrochloric acid. When the beam is now turned on, so rapid is the action and so dense the clouds precipitated, that you could hardly by an effort of attention observe the dark interval which preceded the precipitation of the cloud. This enormous augmentation of the action is due to the presence of the hydrochloric acid. Like the chlorophyl in the leaves of plants, it takes advantage of the loosening of the molecules of nitrite of butyl by the waves of the electric light.

In these experiments we have employed a luminous beam for two different purposes. A small portion of it has been devoted to the decomposition of our vapours, while the great body of the light has served to render luminous the clouds resulting from the decomposition. It is possible to impart to these clouds any required degree of tenuity, for it is in our power to limit at pleasure the amount of vapour in our experimental tube. When the quantity is duly limited, the precipitated particles are at first inconceivably small, defying the highest microscopic power to bring them within the range of vision. Probably their diameters might then be expressed in millionths of an inch. They grow gradually, and as they augment in size, throw from them, by reflexion, a continually increasing quantity of wave-motion, until, finally, the cloud which they form becomes so luminous as to fill this theatre with light. During the growth of the particles the most splendid iridescences are often exhibited. Such I have sometimes seen with delight and wonder in the atmosphere of the Alps, but never anything so gorgeous as those which our laboratory experiments reveal. It is not, however, with the iridescences, however beautiful they may be, that we have now to occupy our thoughts, but with other effects which bear upon the two great standing enigmas of meteorology—the colour of the sky and the polarization of its light.

And here let me briefly say that, were it not for the stimulus imparted to me by the private correspondence of a celebrated man, I should not have entered upon the investigation of these subjects so soon. In reference to the effects of light which you have just witnessed, Sir John Herschel wrote to me thus:—"It is a class of relations eminently calculated to set one thinking, and it seems to have had that effect upon you to excellent purpose. I am glad it has brought you into contact with the blue colour of the sky; still more so if it should lead you to any satisfactory explanation of the polarization of sky-light." The letter went on to treat of "this mysterious and beautiful phenomenon" in a manner which excited in me the strong desire to throw, if possible, some certain light upon a question regarding which the most divergent opinions and speculations were afloat among our most eminent scientific men.

First, then, with regard to the colour of the sky; how is it produced, and can we not reproduce it? This colour has not the same origin as that of ordinary colouring matter, in which certain portions of the white solar light are extinguished, the colour of the substances

being that of the portion which remains. A violet is blue because its molecular texture enables it to quench the green, yellow, and red constituents of white light, and to allow the blue free transmission. A geranium is red because its molecular texture is such as quenches all rays except the red. Such colours are called colours of absorption; but the hue of the sky is not of this character. The blue light of the sky is all *reflected* light, and were there nothing in our atmosphere competent to reflect the solar rays we should see no blue firmament, but should look into the darkness of infinite space. The reflection of the blue is effected by perfectly colourless particles. Smallness of size alone is requisite to ensure the selection and reflexion of this colour. Of all the visual waves emitted by the sun, the shortest and smallest are those which correspond to the colour blue. On such waves small particles have more power than upon large ones, hence the predominance of blue colour in all light reflected from exceedingly small particles. The crimson glow of the Alps in the evening and in the morning is due, on the other hand, to *transmitted* light; that is to say, to light which in its passage through great atmospheric distances has its blue constituents sifted out of it by repeated reflexion.

It is possible, as stated, by duly regulating the quantity of vapour, to make our precipitated particles grow from an infinitesimal and altogether ultra-microscopic size to masses of sensible magnitude; and by means of these particles, in a certain stage of their growth, we can produce a blue which shall rival, if it does not transcend, that of the deepest and purest Italian sky. Let this point be in the first place established. Associated with our experimental tube is a barometer, the mercurial column of which now indicates that the tube is exhausted. Into the tube I introduce a quantity of the mixed air and nitrite of butyl vapour sufficient to depress the mercurial column one-twentieth of an inch; that is to say, the air and vapour together exert a pressure of one six-hundredth of an atmosphere. I now add a quantity of air and hydrochloric acid sufficient to depress the mercury half-an-inch further, and into this compound and highly attenuated atmosphere I discharge the beam of the electric light. The effect is slow; but gradually within the tube arises this splendid azure, which strengthens for a time, reaches a maximum of depth and purity, and then, as the particles grow larger, passes into whitish blue. This experiment is representative, and it illustrates a general principle. Various other colourless substances of the most diverse properties, optical and chemical, might be employed for this experiment. The *incipient cloud* in every case would exhibit this superb blue; thus proving to demonstration that particles of infinitesimal size, without any colour of their own, and irrespective of those optical properties exhibited by the substance in a massive state, are competent to produce the colour of the sky.

But there is another subject connected with our firmament, of a more subtle and recondite character than even its colour. I mean

that "mysterious and beautiful phenomenon,"* the polarization of the light of the sky. The polarity of a magnet consists in its *two-endedness*, both ends, or poles, acting in opposite ways. Polar forces, as most of you know, are those in which the duality of attraction and repulsion is manifested. And a kind of *two-sidedness*—noticed by Huygens, commented on by Newton, and discovered by a French philosopher, named Malus, in a beam of light which had been reflected from one of the windows of the Luxembourg Palace in Paris—receives the name of *polarization*. We must now, however, attach a distinctness to the idea of a polarized beam, which its discoverers were not able to attach to it. For in their day men's thoughts were not sufficiently ripe, nor optical theory sufficiently advanced, to seize upon or express the physical meaning of polarization. When a gun is fired, the explosion is propagated as a wave through the air. The shells of air, if I may use the term, surrounding the centre of concussion, are successively thrown into motion, each shell yielding up its motion to that in advance of it, and returning to its position of equilibrium. Thus, while the *wave* travels through long distances, each individual particle of air concerned in its transmission performs merely a small excursion to and fro.† In the case of sound, the vibration of the air-particles are executed in the direction in which the sound travels. They are therefore called *longitudinal* vibrations. In the case of light, on the contrary, the vibrations are *transversal*; that is to say, the individual particles of æther move to and fro *across* the direction in which the light is propagated. In this respect waves of light resemble ordinary water-waves, more than waves of sound. In the case of an *ordinary* beam of light, the vibrations of the æther particles are executed in *every direction* perpendicular to it; but let the beam impinge obliquely, upon a plane glass surface, as in the case of Malus, the portion reflected will no longer have its particles vibrating in all directions round it. By the act of reflexion, *if it occur at the proper angle*, the vibrations are all confined to a single plane, and light thus circumstanced is called *plane polarized light*.

A beam of light passing through ordinary glass executes its vibrations within the substance exactly as it would do in air, or in æther-filled space. Not so when it passes through many transparent crystals. For these have also their two-sidedness, the arrangement of their particles being such as to tolerate vibrations only in certain definite directions. There is the well-known crystal tourmaline, which shows a marked hostility to all vibrations executed at right angles to the axis of the crystal. It speedily extinguishes such vibrations, while those executed parallel to the axis are freely propagated. The consequence is, that a beam of light, after it has passed through any thickness of this crystal, emerges from it polarized. So also as regards the beautiful crystal known as Iceland spar, or as double doubly refracting spar.

* Herschel's 'Meteorology,' Art. 233.

† 'Lectures on Sound,' p. 3. (Longmans.)

In one direction, but in one only, it shows the neutrality of glass ; in all other directions it splits the beam of light passing through it into two distinct halves, both of which are perfectly polarized, their vibrations being executed in two planes, at right angles to each other.

It is possible by a suitable contrivance to get rid of one of the two polarized beams into which Iceland spar divides an ordinary beam of light. This was done so ingeniously and effectively by a man named Nicol, that the Iceland spar, cut in his fashion, is now universally known as Nicol's prism. Such a prism can polarize a beam of light ; and if the beam, before it impinges on the prism, be already polarized, in one position of the prism it is stopped, while in another position it is transmitted. Our way is now, to some extent, cleared towards an examination of the light of the sky. Looking at various points of the blue firmament through a Nicol's prism, and turning the prism round its axis, we soon notice variations of the brightness of the sky. In certain positions of the spar, and from certain points of the firmament, the light appears to be wholly transmitted ; while, looking at the same points, it is only necessary to turn the prism round its axis through an angle of ninety degrees to materially diminish the intensity of the light. On close scrutiny it is found that the difference produced by the rotation of the prism is greatest when the sky is regarded in a direction at right angles to that of the solar rays through the air. Let me describe a few actual observations made some days ago on Primrose Hill. The sun was near setting, and a few scattered neutral-tint clouds, which failed to catch the dying light, were floating in the air. When these were looked at across the track of the solar beams, it was possible by turning the Nicol round, to see them either as white clouds on a dark ground, or as dark clouds on a bright ground.* In some of its positions the sky-light was in great part quenched by the Nicol, and then the clouds, projected against the darkness of space, appeared white. Turning the Nicol ninety degrees round its axis, the brightness of the sky was restored, and then the clouds became dark through contrast with this brightness.

Experiments of this kind prove that the blue light sent to us by the firmament is polarized, and that the direction of most perfect polarization is perpendicular to the solar rays. Were the heavenly azure like the ordinary light of the sun, the turning of the prism would have no effect upon it ; it would be transmitted equally during the entire rotation of the prism. The light of the sky is in great part quenched, because it is in great part polarized.

When a luminous beam impinges at the proper angle on a plane glass surface it is polarized by reflexion. It is polarized, *in part*, by all oblique reflexions ; but at one particular angle, the reflected light is *perfectly polarized*. An exceedingly beautiful and simple

* I was not aware when these words were written that this observation was made by the indefatigable Brewster.

law, discovered by Sir David Brewster, enables us readily to find *the polarizing angle* of any substance whose refractive index is known. This law was discovered experimentally by Brewster; but the Wave Theory of light renders a complete reason for the law. A geometrical image of it is thus given. When a beam of light impinges obliquely upon a plate of glass it is in part reflected and in part refracted. At one particular incidence the reflected and the refracted portions of the beam are at right angles to each other. The angle of incidence is *then* the polarizing angle. It varies with the refractive index of the substance; being for water $52\frac{1}{2}$, for glass $57\frac{1}{2}$, and for diamond 68 degrees.

And now we are prepared to comprehend the difficulties which have beset the question before us. It has been already stated that in order to obtain the most perfect polarization of the firmamental light, the sky must be regarded in a direction at right angles to the solar beams. This is sometimes expressed by saying that the place of maximum polarization is at an angular distance of 90° from the sun. This angle, enclosed as it is between the direct and reflected rays, comprises both the angles of incidence and reflexion. Hence the angle of incidence, which corresponds to the maximum polarization of the sky, is half of 90° , or 45° . This is the atmospheric polarizing angle, and the question is, what known substance possesses an index of refraction to correspond with this polarizing angle? If we knew this substance, we might be tempted to conclude that particles of it, scattered in the atmosphere, produce the polarization of the sky. "Were the angle of maximum polarization," says Sir John Herschel, " 76° (instead of 90°), we should look to *water*, or ice, as the reflecting body, however inconceivable the existence in a cloudless atmosphere, and a hot summer day, of unevaporated particles of water." But a polarizing angle of 45° corresponds to a refractive index of 1; this means that there is no refraction at all, in which case we ought to have no reflexion. Brewster and others came to the conclusion that the reflexion was from the particles of air themselves. Dr. Rubenson, of Upsala, made the angle enclosed between the direct and reflected beams $90^\circ 2'$; "the half of which," says Mr. Buchan, in his excellent little 'Handy Book of Meteorology,' "is so near the polarizing angle of air, as to leave no doubt that the light of the sky, as first stated by Brewster, is polarized by reflexion from the particles of air." It is difficult to affix a physical meaning to this conclusion. If light be reflected, it must be at the common limiting surface of two media of different refrangibility. But to satisfy the law of Brewster, as Sir John Herschel remarks, "the reflexion would have to be made *in air upon air*!" "The more the subject is considered," adds the celebrated philosopher last named, "the more it will be found beset with difficulties, and its explanation, when arrived at, will probably be found to carry with it that of the blue colour of the sky itself."

If you doubt the wisdom, acknowledge, at all events, the faith in

your capacity which has caused me to bring a subject so entangled before you. I believe, however, that even the intellect which draws its strength and its associations from a totally different source, may have its interest excited in subjects like the present, dark and difficult though they be. I do not expect that you will all grasp the details of this discussion; but I think that everybody present will see the extremely important part hitherto played by the law of Brewster in speculations as to the colour and polarization of the sky. This law leads to the extraordinary conclusion already announced, that the reflexion takes place at the limiting surface of two media of the same refrangibility, where reflexion could no more occur than it could occur in the very heart of an optically homogeneous medium.* I shall now seek to demonstrate in your presence, *firstly*, and in conformation of our former experiments, that sky-blue may be produced by exceedingly minute particles of any kind of matter; *secondly*, that polarization identical with that of the sky is produced by such particles; and *thirdly*, that matter in this fine state of division, where its particles are probably small in comparison with the height and span of a wave of light, releases itself completely from the law of Brewster; the direction of maximum polarization being absolutely independent of the polarizing angle as hitherto defined. Why this should be the case, the wave theory of light, to make itself complete, will have subsequently to explain.

Into this experimental tube, in the manner already described, I introduce a vapour which is decomposable by the waves of light. The mixed air and vapour are sufficient to depress the mercurial column one inch. I add to this mixture air, which has been permitted to bubble through dilute hydrochloric acid, until the column is depressed thirty inches: in other words, until the tube is full. And now I permit the electric beam to play upon the mixture. For some time nothing is seen. The chemical action is doubtless progressing, and condensation going on; but the condensing molecules have not yet coalesced to particles sufficiently large to reflect sensibly the waves of light. As before stated—and the statement rests upon an experimental basis—the particles here generated are at first so small that their diameters would probably have to be expressed in millionths of an inch; while to form each of these *particles* whole crowds of *molecules* are probably aggregated. Helped by such considerations, the intellectual vision plunges more profoundly into atomic nature, and shows us, among other things, how far we are from the realization of Newton's hope that the molecules might one day be seen by microscopes. While

* I am here taking for granted that the polarizing angle of 45° established by observation is rigidly correct. With regard to the reflexion which accompanies atmospheric refraction, inasmuch as the rays are incident upon a convex surface, or upon a series of concentric convex surfaces, the reflected light is dispersed in space instead of reaching the eye of the observer. Such reflexion, moreover, even to an eye in space, would not account for the colour of the sky, nor probably for the quantity of its light.

I am speaking, you observe this delicate blue colour forming and strengthening within the experimental tube. No sky-blue could exceed it in richness and purity; but the particles which produce this colour lie wholly beyond our microscopic range. A uniform colour is here developed, which has as little breach of continuity—which yields as little evidence of the particles concerned in its production—as that yielded by a body whose colour is due to true molecular absorption. This blue is at first as deep and dark as the sky seen from the highest Alpine peaks, and for the same reason. But it grows gradually brighter, still maintaining its blueness, until at length a whitish tinge mingles with the pure azure; announcing that the particles are now no longer of that infinitesimal size which reflects the shortest waves alone.*

The liquid here employed is the iodide of allyl,† but I might choose any one of a dozen substances here before me to produce the effect. You have seen what may be done with the nitrite of butyl. With nitrite of amyl, bisulphide of carbon, benzol, benzoic æther, &c. the same blue colour may be produced. In all cases where matter slowly passes from the molecular to the massive state, the transition is marked by the production of the blue. More than this:—you have seen me looking at the blue colour (I hardly like to call it a blue “cloud,” its texture and properties are so different from ordinary clouds) through this bit of spar. This is a Nicol’s prism, and I could wish one of them to be placed in the hands of each of you. Well, this blue that I have been regarding turns out to be, if I may use the expression, a bit of more perfect sky than the sky itself. When I look across the illuminating beam exactly as we look across the solar rays in the atmosphere, I obtain not only partial polarization, but *perfect* polarization. In one position of the Nicol the blue light seems to pass unimpeded to the eye; in the other it is absolutely cut off, the experimental tube being reduced to optical *emptiness*. Behind the experimental tube it is well to place a black surface, in order to prevent foreign light from troubling the eye. In one position of the Nicol this black surface is seen without softening or qualification; for the particles within the tube are themselves invisible, and the light which they reflect is quenched. If the light of the sky were polarized with the same perfection, on looking properly towards it through a Nicol we should meet, not the mild radiance of the firmament, but the unilluminated blackness of space.

The construction of the Nicol is such that it permits to pass through it vibrations which are executed in a certain determinate direction, and these only. All vibrations executed at right angles to this direction are completely stopped: while components only of those executed obliquely to it are transmitted. It is easy, therefore, to see

* Possibly a photographic impression might be taken long before the blue becomes visible, for the ultra-blue rays are first reflected.

† For which I have to thank the obliging kindness of Dr. Maxwell Simpson, F.R.S.

that from the position in which the Nicol must be held to transmit or to quench the light of our incipient cloud, we can infer the direction of the vibrations of that light. You will be able to picture those vibrations without difficulty. Suppose a line drawn from any point of the "cloud" perpendicular to the illuminating beam. The particles of æther along that line, which carry the light from the cloud to the eye, vibrate in a direction perpendicular both to the line and to the beam. And if any number of lines be drawn in the same way from the cloud, like the spokes of a wheel, the particles of æther along all of them oscillate in the same manner. Wherefore, if a *plane surface* be imagined cutting the incipient cloud at right angles to its length, the perfectly polarized vibrations discharged laterally will all be parallel to this surface. This, in fact, is the plane of vibration of the polarized light. Or you may suppose a circle drawn round the experimental tube, and a series of strings attached to various points of this circle. If all the cords be stretched as perpendiculars to the experimental tube, and caused to wriggle by a series of jerks imparted at right angles both to them and to the tube, the motion of the particles of the strings will then represent those of the particles of æther. A distinct image of those vibrations is now, I hope, within the reach of every person here present.

Our incipient blue cloud is a virtual Nicol's prism, and, between it and the real Nicol, we can produce all the effects obtainable between the polarizer and analyzer of a polariscope. When, for example, a thin plate of selenite, which is crystallized sulphate of lime, is placed between the Nicol and the incipient cloud, we obtain the splendid chromatic phenomena of polarized light. The colour of the gypsum-plate, as many of you know, depends upon its thickness. If this be uniform, the colour is uniform. If, on the contrary, the plate be wedge-shaped, thickening gradually and uniformly from edge to back, we have brilliant bands of colour produced parallel to the edge of the wedge. Perhaps the best form of plate for experiments of this character is that now in my hand, which was prepared for me some years ago by a man of genius in his way, the late Mr. Darker of Lambeth. It consists of a plate of selenite thin at the centre, and gradually thickening towards the circumference. Placing this film between the Nicol and the cloud, we obtain, instead of a series of parallel bands, a system of splendidly coloured rings. The colours are most vivid when the incipient cloud is looked at perpendicularly. Precisely the same phenomena are observed when we look at the blue firmament in a direction perpendicular to the solar rays.

We have thus far illuminated our incipient cloud with ordinary light, and found the portion of this light reflected laterally from the cloud in all directions round it to be perfectly polarized. We will now examine the effects produced when the light which illuminates the cloud is itself polarized. In front of the electric lamp, and between it and the experimental tube, is placed this fine Nicol's prism, which is sufficiently large to embrace and to polarize the entire beam.

The prism is now placed so that the plane of vibration of the light emergent from it, and falling upon the cloud, is vertical. How does the cloud behave towards this light? This formless aggregate of infinitesimal particles, without definite structure, shows the two-sidedness of the light in the most striking manner. It is absolutely incompetent to reflect upwards or downwards, while it freely discharges the light horizontally, right and left. I turn the polarizing Nicol so as to render the plane of vibration horizontal; the cloud now freely reflects the light vertically upwards and downwards, but it is absolutely incompetent to shed a ray horizontally to the right or left.

Fix your attention upon one of those reflecting particles. Figure it as a little sphere with the beam of the electric light impinging upon it. Let us call that diameter which coincides with the direction of the beam, the *axis* of the sphere; one of its *poles* would then be turned towards the light, and the other in the opposite direction. The equator of the little sphere would of course be midway between its poles. Now, conceive a parallel of latitude drawn upon the sphere at an angular distance of 45 degrees from the pole; that is to say, midway between the pole and the equator. Then what occurs with ordinary light is this: all the vibrations tangent to the little circle, which I have called a parallel of latitude, are reflected perfectly polarized; but all vibrations executed at right angles to the circle go unreflected through the little sphere. If, instead of ordinary light, we use polarized light, it is clear that at two opposite points of the little circle the vibrations are executed along the tangents, while at two other opposite points they are executed at right angles to the tangents. In the former case the particle *reflects* the light, in the latter it *transmits* the light unreflected. What is true of a single particle is true of all, and hence the inability of the incipient cloud formed of such particles to reflect light in two directions, while it freely reflects it in two others. The entire facts are now placed before you. The reflecting particle and the waves of æther are of course both beyond the range of the senses, but to the intellect the conceptions here introduced are just as easy as if, in illustration, I had pointed to the poles, equator, and parallel of latitude of an ordinary terrestrial globe.

Suppose the atmosphere of our planet to be surrounded by an envelope impervious to light, with an aperture on the sunward side, through which a solar beam could enter and cross our atmosphere. Surrounded on all sides by air not directly illuminated, the track of the sunlight would resemble that of the electric beam in a dark space filled with our incipient cloud. The course of the sunbeam would be *blue*, and it would discharge laterally, in all directions round it, light in precisely the same polarized condition as that discharged from the incipient cloud. In fact, the azure revealed by the sunbeam would be the azure of such a cloud. And if, instead of permitting the ordinary light of the sun to enter the aperture, a Nicol's prism were placed there, which should polarize the sunlight on its entrance into our atmosphere, the particles producing the colour of the sky

would act precisely like those of our incipient cloud. In two directions we should have the solar light reflected; in two others unreflected. In fact, out of such a solitary beam, traversing the unilluminated air, we should be able to extract every effect shown by our incipient cloud. In the production of such clouds we virtually carry bits of the sky into our laboratories, and obtain with them all the effects obtainable in the open firmament of heaven.

And here, had not a sufficient strain been already imposed upon your minds, I might enter upon the description of a series of extraordinary effects observed when the particles of our incipient clouds are allowed to augment in size, so as to approach the condition of true cloudy matter. The selenite ring-system, already referred to, is a most delicate reagent for the detection of polarized light. When we look *normally*, or perpendicularly, at an incipient cloud, the colours of the rings are most vividly developed, a diminution of the colour being immediately apparent when the incipient cloud is regarded *obliquely*. But let us continue to look through the Nicol and selenite normally at the cloud: the particles augment in size, the cloud becomes coarser and whiter, the strength of the selenite colours becoming gradually feebler. At length the cloud ceases to discharge polarized light along the normal, and then the selenite colours entirely disappear. If *now* the cloud be regarded *obliquely*, the colours are restored, very vividly, if not with their first vividness and clearness. Thus the cloud that has ceased to discharge polarized light at right angles to the illuminating beam, pours out such light copiously in oblique directions. The direction of maximum polarization changes with the texture of the cloud.

But this is not all; and to understand, even partially, what remains, a word must be said regarding the appearance of the colours of our plate of selenite. If, as before stated, the plate be of uniform thickness, its hue in polarized light is uniform. Suppose, then, that by arranging the Nicol the colour of the plate is raised to its maximum brilliancy, and suppose the colour produced to be *green*; on turning the Nicol round its axis the green becomes fainter. When the angle of rotation amounts to 45 degrees the colour disappears; we then pass what may be called a neutral point, where the selenite behaves, not as a crystal, but as a bit of amorphous glass. Continuing the rotation, a colour reappears, but it is no longer green, but *red*. This attains its maximum at a distance of 45 degrees from the neutral point, or, in other words, at a distance of 90 degrees from the position which showed the green at its maximum. At a further distance of 45 degrees from the position of maximum red, the colour disappears a second time. We have there a second neutral point, beyond which the green comes again into view, attaining its maximum brilliancy at the end of a rotation of 180 degrees. By the rotation of the Nicol, therefore, through an angle of 90 degrees, we produce a colour *complementary* to that with which we started.

As may be inferred from this result, the selenite ring-system

changes its character when the Nicol is turned. It is possible to have the centre of the circle dark, the surrounding rings being vividly coloured. The turning of the Nicol through an angle of 90 degrees renders the centre bright, while every point occupied by a certain colour in the first instance is occupied by the *complement* of that colour in the second. But what am I aiming at in these long preliminary statements? I want to be able to say, with full assurance of being understood by everybody present, that a cloud may so alter its texture as to produce upon light an effect equivalent to the rotation of the Nicol through 90 degrees. By curious internal actions, not here to be described, the cloud in our experimental tube sometimes divides itself into sections of different textures. Some sections are coarser than others, while it often happens that some are iridescent to the naked eye, and others not. Looking normally at such a cloud through the selenite and Nicol, it often happens that in passing from section to section the whole character of the ring-system is changed. You start with a section producing a *dark* centre and a corresponding system of rings; you pass to another section through a neutral point, and find in that section the centre *bright*, and at the same radial distances find each of the first rings displaced by one of the complementary colour. Sometimes as many as four such reversions occur in the cloud of an experimental tube a yard long. Now, the changes here indicated mean that in passing from section to section of the cloud the plane of vibration of the polarized light turns suddenly through an angle of 90 degrees; this change being entirely due to the different texture of the two parts of the cloud.

You will now be able to understand, as far as it is capable of being understood, a very beautiful effect which, under favourable circumstances, might be observed in our atmosphere. This experimental tube contains an inch of the iodide of allyl vapour, the remaining 29 inches necessary to fill the tube being air, which has bubbled through aqueous hydrochloric acid. Besides, therefore, the vapour of iodide of allyl, we have those of water and of acid within the tube. The light has been acting on the mixture for some time, a beautiful incipient blue cloud being formed. As before stated, the "incipient cloud" is wholly different in texture and optical properties from an ordinary cloud; but it is possible to precipitate the aqueous vapour within this tube so as to cause it to form a cloud similar to the clouds of our atmosphere. This new and real cloud will be precipitated in the midst of the azure of the incipient cloud. An exhausted vessel of about one-third of the capacity of the experimental tube is now connected with the tube, the passage uniting both being closed by a stop-cock. On opening this cock the mixed air and vapour will rush from the experimental tube into the empty vessel; and, in consequence of the chilling due to rarefaction, the vapour in the experimental tube will fall together as a true cloud. You are now prepared for the experiment. I first look at this blue colour, so as to obtain a vivid ring-system with a dark centre. Turning on the cock, the air is rarefied

and the cloud precipitated. What is the result? Instantly the centre of the system of coloured rings becomes bright, and the whole series of colours corresponding to definite radial distances, complementary. While I continue to look at the cloud, it gradually melts away as an atmospheric cloud might do in the azure of heaven. And *there* is our azure also remaining behind. The coarser cloud seems drawn aside like a veil, the blue reappears, the first ring-system, with its dark centre and correspondingly coloured circles, being restored.

Thus patiently and bravely you have accompanied me over a piece of exceedingly difficult ground; and I think as a prudent guide, we ought to halt upon the eminence we have now attained. We might go higher, but the boulders begin here to be very rough. At a future day we shall, I doubt not, be able to overcome this difficulty, and to reach together a greater elevation.

[J. T.]

Friday, March 19, 1869.

ADMIRAL SIR HENRY JOHN CODRINGTON, K.C.B., Manager,
in the Chair.

DR. A. CRUM BROWN, F.R.S.E.

On Chemical Constitution, and its Relation to Physical and Physiological Properties.

CHEMISTS have long endeavoured to answer the question, What is the relation in which the constituents stand to one another in a compound? and numerous hypotheses more or less ingenious have been devised for this purpose. Two of these modes of representing chemical phenomena occupy so prominent a place in the history of the science as to merit special notice, even in so slight and hurried a sketch as this must be. These are, 1st, the Electro-chemical and Radical Theory; and 2nd, the Theory of Atomicity and Chemical Structure.

The first was the product of the genius, learning, and laborious research of Berzelius; it was soon adopted by all chemists, and formed for many years the foundation of all chemical teaching and the guide in all chemical work. The point of view from which it regards chemical phenomena is that of combination and decomposition, of the union of elements to form compounds and the separation of compounds into elements. A very important form of chemical decomposition is electrolysis, or the breaking up of a compound by means of current electricity. From the nature of the case electrolysis gives rise to a dichotomous decomposition, and this duality was extended to all cases of combination and decomposition. Elements combine with each other in pairs; these pairs may again combine in pairs, forming compounds of the second order, and so on. Thus calcium combines with oxygen to form lime, sulphur combines with oxygen to form sulphuric acid, and sulphuric acid combines with lime to form sulphate of lime. This union of compounds with compounds was not supposed to depend on a union of the constituents of the one with the constituents of the other, but to be a combination of the one as a whole with the other as a whole; not a combination of the calcium of the lime with the sulphur or with the oxygen of the sulphuric acid, or of the sulphur of the sulphuric acid with the oxygen of the lime, but of the lime as such with the sulphuric acid as such.

This view may be illustrated by a reference to the relations of human life. Individuals unite to form partnerships or corporations, and these may again enter into alliances, although the members of the

one allied corporation may be altogether unacquainted and unconnected with the members of the other.

But the progress of discovery brought to light facts which seemed to contradict this view of binary combination. Cases were observed in which a compound of two elements united directly with an element, and to meet this new class of facts the theory was modified by the introduction of the notion of Radicals. A Radical was a compound which acts like an element.

The simile introduced above may be used to illustrate this extension of the theory. Some combinations of men (corporations) can be treated as individuals, can enter into legal relations with individuals, while others cannot; so some compounds can unite with elements, while others have not this capability.

The Theory of Atomicity regards chemical phenomena from an altogether different point of view. In it the various substances are considered as modifications of one another rather than as compounds. The rise of this mode of viewing chemical phenomena may be traced from the early papers by Dumas, and by Laurent, on Substitution. It appears more prominently in the position given to double decomposition as the representative of all chemical action, by Laurent and Gerhardt, in the types of Gerhardt and Williamson, in Frankland's theory of the organo-metallic bodies, and in its extension by Kolbe to the compounds of carbon. It was reserved, however, for Kekulé to combine these ideas into a consistent theory.* The theory has been further elaborated by Butlerow, to whom we owe the name "Chemical Structure," by Erlenmeyer, and by many others, and it has been adopted and applied with slight modifications by almost all chemists engaged in organic research.

According to this theory the typical form of chemical action is what we may call the *chemical exchange*. To illustrate this idea we may consider the simplest case; that of double decomposition where two molecules act on one another to produce two new molecules.

Chloride of sodium, for instance, acts on nitrate of silver, producing chloride of silver and nitrate of sodium. Comparing chloride of sodium and chloride of silver, we at once see that while there are important respects in which the sodium and the silver differ as to the nature of their union with chlorine (thus the amount of work required to separate the metal from the chlorine is very different in the two cases) still, from one point of view (and that is the point of view taken by the atomicity theory), the silver may be said to replace or to be substituted for the sodium. In the same way a cup filled with mercury is very different from the same cup filled with water; and the relation of the mercury to the cup differs in many respects (such as pressure

* It is right to observe that although Kekulé has used this theory with the most eminent success, both in the explanation of facts already known, and in the discovery of new chemical relations, he does not exclude the possibility of the union of compounds with each other to form compounds of a second order.

and adhesion) from the relation of the water to the cup; but they agree in this, that the cup is *filled* in both cases. In the same way the chlorine is said to be *saturated* by the sodium or the silver, although the intimacy or firmness of the combination is not the same in the two cases.

We may also consider this double decomposition from the other side. As the silver and sodium have changed places, so the chlorine has changed place with the *rest* of the nitrate of silver—with what in the nitrate of silver is not silver; or, representing the action in symbols ($\text{NaCl} + \text{AgNO}_3 = \text{AgCl} + \text{NaNO}_3$) Cl and NO_3 have changed places.

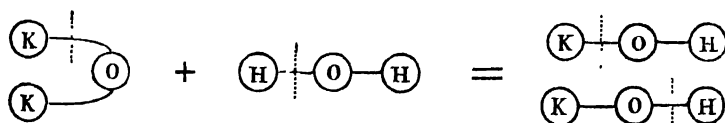
In this example we have one atom or group replacing one other atom or group; but all cases of double decomposition are not of so simple a kind. Thus, when water is treated with pentachloride of phosphorus we find that *one* atom of oxygen (from the water) replaces, and is replaced by, *two* atoms of chlorine from the pentachloride; thus, $\text{PCl}_5 + \text{H}_2\text{O} = \text{PCl}_3\text{O} + 2 \text{HCl}$. So that while the two atoms of hydrogen were formerly united to one atom of oxygen and formed with it one molecule, they are, after the change, each united to a separate atom of chlorine and form with them two molecules.

Oxygen, therefore, in this case (and, as far as we know, in all cases) enters into two relations, while hydrogen, chlorine, silver, and sodium only enter into one. In a similar way it has been shown that the different elements have different "atomicities" or enter into different numbers of relations. It is to this "polyatomicity," or *multiple-relatedness*, that the complexity of compounds is due; for it is obvious that by the union together of several multiply related atoms a very complicated structure may be produced.

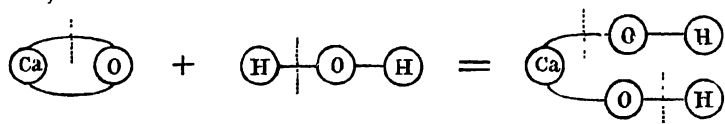
In the case of a compound containing only two atoms, such as chloride of sodium, there is clearly only one way in which it can break into residues; but a complex substance containing many atoms may, and generally does, break in different ways when acted on by different substances; and it is by the study of these ways of decomposition of a substance, and by the study of the ways in which by means of double decomposition it can be produced, that we arrive at a knowledge of its structure, that is, of the mutual relation of its atoms.

But the multiple-relatedness of some atoms produces a further complication, producing a kind of chemical action, which, while still a chemical exchange, cannot be called double decomposition. In double decomposition we saw that each molecule breaks into residues which change places with the residues of the other molecule, and that this breaking into residues results from the rupture of one or more relations between pairs of atoms. But where we have multiply-related atoms, it may happen that such a rupture takes place without a separation of the residues, these being retained in combination by some other relation of their multiply-related atoms. To illustrate this we may compare the action of anhydrous potash, K_2O , and of anhydrous lime, CaO , on water.

Using graphic formulæ, we have in these two cases:—



And,



Here the dotted lines indicate the relations ruptured; and it will be seen that, while in the first case the rupture produces a separation into two residues, in the second case it does not; what would otherwise be residues remaining united, on account of the double-relatedness of the calcium atom.

From this examination of chemical exchange, it will be obvious that no operation of this kind can produce a change in the "atomicity" of an atom; for, for every relation ruptured, a new one is entered into. But we have no reason to suppose that all chemical action is of this kind; and there are numerous phenomena which it is very difficult to explain, except by the assumption that there is another kind of chemical action, in which the number of relations of an atom is increased or diminished. Such actions are those by which we pass from one series of compounds to another. Thus the ferrous salts are connected together by processes of exchange; but it is only by making new hypotheses that we can thus explain the passage from the ferrous to the ferric salts. Similar relations exist between the manganous salts, the manganic salts, the manganates, and the permanganates, where a consideration of each group, apart from the others, would lead us to a different atomicity for manganese; and many other examples might be given of the same kind. The speaker considered it, in the mean time, to be better to regard each such series separately, rather than, by an attempt to bring all chemical processes under one class, to endanger the stability of the theory of chemical structure which, while it is probably not destined, in its present form, to remain as a permanent part of the great edifice of the science, is certainly a most convenient scaffolding, not easy to replace, and not hastily to be thrown down.

Having thus seen what is meant by chemical structure, and how we arrive at a knowledge of it by a study of the *history* of the substance, of the ways in which it may be formed and in which it may be decomposed; we may now glance at the relations which exist between the chemical structure of a substance and its physical and physiological properties. We shall consider specially two of the physical characters of matter, volatility and colour, and examine in what way these are modified by the performance upon the substance of certain specified

chemical operations. The volatility of a substance depends upon two things:—1st, the temperature at which the substance boils under a particular pressure; and, 2nd, the change of boiling-point produced by a change of pressure. In order, therefore, fully to know the volatility of a substance, its boiling-point must be determined through a very great range of pressure. This involves great labour; and only a few substances have been thus fully examined. Almost all we know on this interesting question is due to the ingenious and patient experiments of Regnault. These do not, as yet, furnish us with sufficient data to enable us to deduce anything like a law. They show us, however, that a mere comparison of boiling-points under an arbitrarily-selected pressure (such as 760 millimètres, which happens to be the mean pressure of the atmosphere) cannot lead us to a law, as the boiling-points of two substances are frequently changed very unequally by a change of pressure.

Such comparisons of boiling-points have been made, and from them have been deduced, especially by Kopp, a series of very interesting, and certainly not fortuitous coincidences. That distinguished chemist and physicist has shown that, in a very large number of instances, the same change of chemical structure produces nearly the same change of boiling-point. These "laws" of Kopp are only approximate, and are not even approximate in the cases where the boiling-points of the substances compared are very differently changed by change of pressure.

Turning to the other physical character which has been mentioned, namely colour, we see at once a marked regularity. As a rule, substances belonging to the same series differ from one another in degree rather than in kind of colour; while in passing from one series to another, we observe that the colour undergoes a total change of character. This is well illustrated by comparing the colours of substances belonging to such series as the ferrous salts, the ferric salts, the ferrates; the manganous salts, the manganic salts, the manganates and the permanganates; the cuprous and cupric salts, the chromous and chromic salts, the chromates and perchromic acid. Possibly such changes of colour as we see in the transformation of rosaniline and its derivatives into leukaniline and analogous bodies, and of blue into white indigo, may be cases of the same kind. It is also interesting to note, that while the nitro-substitution products of the aromatic series are generally yellow, all the known substances of the same kind in the fatty series are colourless.

These considerations of colour would naturally incline us to regard the operations which lead from one series to another as different in kind from those which lead from one member to another of the same series; and when we examine the physiological action of bodies of the same, and of different series, this impression is greatly strengthened.

The speaker described in some detail a few of the observations made within the last two years by Dr. T. R. Fraser and himself,

pointing out the similarity of the action of substances belonging to the same series, and the remarkable change of physiological action produced by those chemical changes which lead from one series to another. The illustrations were drawn from the natural alkaloids—a group of substances containing trebly-related nitrogen, and those derivatives of the alkaloids which contain fivefold-related nitrogen. It was shown that the salts of the alkaloids, although containing fivefold-related nitrogen, were not adapted for this comparison, on account of the readiness with which they lose acid in the presence of alkaline substances, their nitrogen thus returning to the trebly-related condition. The bodies formed by the addition of a compound of methyl have not this disadvantage; and as the nitrogen in them is *permanently* fivefold-related, their physiological action may be satisfactorily compared with that of the alkaloids themselves.

The experiments leading to a knowledge of the action of strychnia and of the salts of methyl-strychnium were described; and it was shown that while the former acts by *exciting* the *origins* of the motor nerves in the spinal cord, the latter act by *diminishing the action* and ultimately paralyzing the *terminations* of the same nerves in the muscles. Similar relations exist between brucia and methyl-brucium, thebaia and the salts of methyl-thebaidium, morphia and the salts of methyl-morphium, &c. Indeed, it may be stated generally that, as far as observation goes, compounds of trebly-related nitrogen exert an action totally different in kind from similar compounds of fivefold-related nitrogen, that a similar difference exists between the triatomic and pentatomic compounds of other members of the nitrogen family, and that this principle appears to be of still wider, and probably general, application.

The speaker, in conclusion, drew attention to the peculiar interest attaching to those regions of science which lie on the frontiers between two distinct departments, as on their successful exploration would depend the ultimate fusion of all physical sciences into one, the science of dynamics, the science which treats of matter and energy, and their relations to one another. Such a fusion is probably very remote; but we now see in the border-land between chemistry and physics that slow process of absorption going on which has already converted the once independent sciences of sound, light, heat, electricity, and magnetism into more or less completely subjugated provinces of the great empire of applied mathematics. If we believe in the unity of the plan of creation we must believe that this process will advance and ultimately triumph.

[A. C. B.]

Friday, May 14, 1869.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

W. H. PERKIN, Esq. F.R.S.

On the Newest Colouring Matters.

SEVEN years ago the subject of the Coal-tar Colours was first brought under your notice in this Institution by the illustrious Dr. Hofmann, whose brilliant lecture on Mauve and Magenta must still be fresh in your memories. Since then your attention has been directed to a further development of the same subject by Mr. Frederick Field; and it may appear strange that I should invite you after so short an interval to listen to another discourse on the chemistry of the artificial colouring matters. I need not remind you, however, that in this age of progress the most remarkable advances are those which are assisted by the hand of science; and the bare statement that the progressiveness of scientific work is strikingly exemplified by the history of these colouring matters will, I trust, be deemed a sufficient justification of my review of the subject.

The first of the coal-tar colours, the "Mauve," came before the world nearly thirteen years ago; the "Magenta" appeared about two years later; and each succeeding year has seen additions to this remarkable class of products. Indeed so rapidly have these colours multiplied, that I can only notice the chief points of interest in their chemical history.

I may remind you that coal-tar is produced in the manufacture of illuminating gas by the destructive distillation of coal, and that it consists of a host of products, from a few of which our coal-tar colours are derived. Many of these colours are derivatives of *aniline*, one of the organic bases found in coal-tar. The separation of this base from the other coal-tar products is attended with much difficulty, and for this reason the whole of the aniline employed in the manufacture of colouring matters is prepared from the more volatile product *benzol*. By the action of nitric acid the *benzol* is converted into a dense yellow oil called *nitro-benzol*, and by the action of nascent hydrogen this new compound is transformed into aniline. The *benzol* of commerce, however, is invariably a mixture of *benzol* and *toluol*, and the product

obtained from it is a mixture of the allied bases aniline and *toluidine*, both of which are required for the formation of the artificial colouring matters. The commercial aniline thus constituted is an oily liquid usually of a pale sherry colour. It dissolves readily in dilute acids, forming nearly colourless solutions, which yield when treated with bichromate of potassium a sooty black powder. This unpromising product contains that beautiful colouring matter the Mauve, which may be extracted by dilute spirit of wine.

As the Mauve is the oldest of the coal-tar colours, and a child of my own, I feel constrained to say something about its peculiarities. I may remind you in the first place that it is characterized by great stability, a quality not shared by all the coal-tar purples. The pure colouring matter contains a powerful organic base now called *mauveine*. This base dissolves in spirit of wine, forming a solution of a dingy violet colour, and the development of the beautiful mauve or purple is the result of the union of the base with an acid. The colouring matter generally used is the acetate of mauveine, a salt which may be obtained in fine crystals having a green metallic lustre. So great is the affinity of mauveine for even the most feeble acids, that the dull colour of its alcoholic solution rapidly changes to purple under the influence of the carbonic acid of the breath. Mauveine is decolorized by nascent hydrogen, but its original colour is instantaneously restored by the oxygen of the air. Ordinary indigo is similarly affected, but it does not resume its colour as rapidly as mauveine.

As early as 1836, Runge obtained from the products of the destructive distillation of coal a basic oil, which exhibited a remarkable blue coloration when treated with chloride of lime. This oil, which he named *kyanol*, or blue oil, was afterwards found to be aniline; and since the discovery of the mauve, the blue coloration produced by chloride of lime has often been ascribed to the formation of that colouring matter. I have lately succeeded in obtaining the product of Runge's experiment in the solid condition, and I find that it dissolves in alcohol, forming a solution of a nearly pure blue colour, which is changed to a brownish-red by the action of caustic alkali. It, therefore, differs essentially from the mauve, an alcoholic solution of which when treated with caustic alkali passes from purple to violet. The blue product, which I propose to call "Runge's Blue," undergoes a very remarkable change when subjected to the action of heat. It is rapidly converted into a purple colouring matter, which is found to be the true mauve. Indeed Runge's blue is so prone to change into the more stable mauve that its composition cannot be satisfactorily determined.

The beautiful crystalline colouring matter Magenta, and its base *rosaniline*, have been brought under your notice, with ample illustrations of their formation and properties, on previous occasions. I shall not stop, therefore, to recount the chemical history of these important compounds, but will proceed to develop the principles which elucidate the structure of the artificial colouring matters. I

may remark, however, that rosaniline now occupies much the same position with respect to the coal-tar colours as aniline occupied formerly. It is now the principal raw material in the manufacture of these colouring matters.

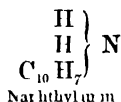
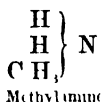
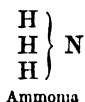
Nearly all the coal-tar colours contain organic bases which may be regarded as representatives of *ammonia*. It is scarcely necessary to remind you that this typical body ammonia is composed of three atoms of hydrogen and one atom of nitrogen, its symbolic formula being H_3N . Chemists have found that certain groups of carbon and hydrogen atoms can take the place of single atoms of hydrogen in chemical compounds. These groups are called radicals, and many of them are distinguished by special names; thus we have the radicals

CH_3 Methyl

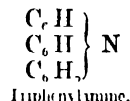
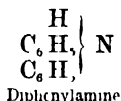
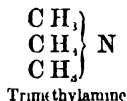
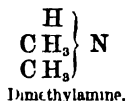
C_6H_5 Phenyl

C_{10}H_7 Naphthyl

each of which has the combining value of an atom of hydrogen. Now we can take ammonia and by chemical means insert any one of these radicals in the place of hydrogen, so as to produce a complex form of ammonia. With the radicals I have mentioned we may get this series of compounds :



Phenylaniline is merely the systematic name for aniline; so you see we actually start with an ammonia in the preparation of our colouring matters. The process of displacing hydrogen may be continued until we get ammonias in which compound radicals are substituted for two-thirds or even the whole of the hydrogen. We have thus obtained the compounds—



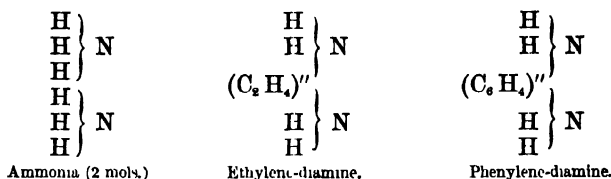
In addition to those radicals, like methyl and phenyl, which displace single atoms of hydrogen, we have other groups of carbon and hydrogen atoms, called bivalent radicals, each of which can displace two atoms of hydrogen. The formulæ and names of two radicals of this class are here given, dashes being used to indicate the combining value :

$(\text{C}_2\text{H}_4)''$ Ethylene

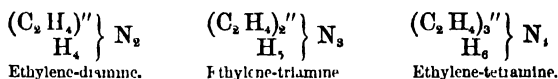
$(\text{C}_6\text{H}_4)''$ Phenylene

Now when we attempt to displace the hydrogen of ammonia by one of these radicals, we obtain a very remarkable result. Instead of taking the place of two atoms of hydrogen in a single molecule of ammonia, the radical acts upon two molecules, displacing a single atom of each

and binding together the residues, so as to produce a double ammonia or *diamine*, thus :

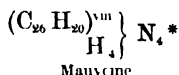


By means of these bivalent radicals we may thus bind three molecules of ammonia together and obtain a triple ammonia or *triamine*; and we may even bind four molecules together and produce a quadruple ammonia or *tetramine*. The formulæ of these complex ammonias may be written in a comparatively simple manner, thus :

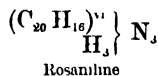


Most of the bases of our coal-tar colours are compounds of this class.

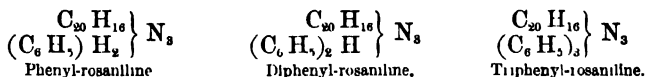
Mauveine, the base of the mauve, appears to be a tetramine in which the group $\text{C}_{26} \text{H}_{20}$ takes the place of eight atoms of hydrogen. This group really consists of several radicals, but it may be conveniently represented as an integral part of the formula, thus :



Rosaniline, the base of the magenta, is undoubtedly a triamine, in which the place of six atoms of hydrogen is filled by the group $\text{C}_{20} \text{H}_{16}$, also consisting of several radicals, which need not be written separately for our present purpose. We accordingly represent the anhydrous base by the formula



If we boil a salt of rosaniline with aniline or phenylamine we find that the radical phenyl displaces the hydrogen that is not combined with carbon, and we obtain successively salts of three new bases which may be thus formulated :



* From recent experiments I am induced to consider the formula of Mauveine as $\text{C}_{26} \text{H}_{24} \text{N}_4$, instead of $\text{C}_{27} \text{H}_{24} \text{N}_4$.

These successive substitutions of phenyl for hydrogen are attended with remarkable alterations of colour. The beautiful red or magenta colour of the rosaniline salt is changed first to violet, then to blue violet, and lastly to a magnificent blue. The salts of triphenyl-rosaniline constitute the important colouring matter which is known commercially as "*Bleu de Lyon*" or "Opal Blue," while the salts of the other two bases form the beautiful product called "*Violet Impériale*." The remarkable relationship of these colouring matters to rosaniline was elucidated by Dr. Hofmann.

But phenyl is not the only radical that can be substituted for hydrogen in a complex molecule, and Dr. Hofmann has succeeded in producing methyl and ethyl rosanilines analogous to the phenyl derivatives. By heating rosaniline with *iodide of methyl* we displace one hydrogen atom by the group CH_3 and obtain *methyl-rosaniline*, a base which forms salts of a red violet colour. By the further action of the iodide of methyl a second hydrogen atom is displaced, and we get *dimethyl-rosaniline*, the salts of which exhibit a bluer shade of violet. A third substitution of methyl for hydrogen gives us *trimethyl-rosaniline*, which forms salts of a very blue violet colour. The methyl and ethyl derivatives of rosaniline are the bases of the magnificent colouring matters known as the "Hofmann Violets," and extensively used by the dyer and the printer.

I may mention at this point that up to the present time I have only been able to effect a single substitution of methyl for hydrogen in mauveine. The most remarkable fact connected with this substitution is, that the methyl influences the colour of the product in the opposite manner to that observed in the case of rosaniline; instead of making the colour bluer it causes it to become redder.

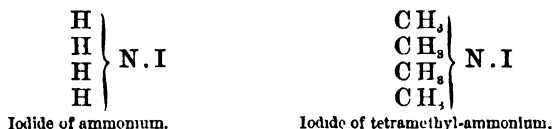
Our theoretical considerations must now be interrupted, as I have to call your attention to a few colouring matters upon which chemistry has thrown but little light as yet.

Oil of turpentine when treated with bromine and water yields a very peculiar viscid body having the composition $\text{C}_{10}\text{H}_{15}\text{Br}_3$. I found that when this product was heated with a solution of rosaniline in methylated spirit, purple and violet colouring matters of great beauty were produced. These colours are now very extensively used by the dyer and printer, being commercially known as the "Britannia Violets." They appear to be amorphous and are easily fusible, consequently they are not very promising subjects for chemical investigation.

The next colouring matter that comes under our notice is another derivative of rosaniline. When experimenting with rosaniline, M. Lauth found that a solution of this base in concentrated sulphuric acid reacted with the colourless and volatile liquid called *aldehyd* to form a beautiful blue colouring matter. Unfortunately this product was characterized by great instability, a quality not generally desirable in a colour. A dyer named Chirpin endeavoured to turn this blue to practical account, but all his attempts to render it permanent

were fruitless. He happened, however, to mention his difficulty to a friendly photographer, who having unbounded faith in the powers of the chemicals employed in his own art, confidently recommended hyposulphite of sodium as a fixing agent. Though the connection between the fixing of a dye and the fixing of a photograph was not sufficiently obvious to inspire hope, the dyer resolved to test the efficacy of his friend's hyposulphite. Much to his astonishment he found that the salt turned his useless blue into a splendid green, which fortunately proved to be a fast colour. This is the history of the beautiful colouring matter known as the "Aldehyd Green," or "Night Green," the latter name having been applied to it on account of its brilliancy under artificial light. Though its chemical nature is not perfectly understood, there can be no doubt that it is the salt of a colourless organic base capable of decomposing ammonia salts.

We must now resume the consideration of our compound ammonias. I have told you that all the hydrogen in ammonia may be displaced by compound radicals, and have referred to trimethylamine as a product of this complete displacement. These complex forms of ammonia were studied by Wurtz and Hofmann, but more particularly by the latter, whose magnificent researches in connection with these bodies have secured him an exalted position among modern chemists. Having succeeded in displacing the whole of the hydrogen in ammonia, Dr. Hofmann naturally thought that the substitution process could be carried no further; but disregarding preconceived ideas, he submitted his altered ammonias to the action of the iodides of methyl and ethyl. He found to his astonishment, that a compound ammonia, like trimethylamine, would unite with the iodide to produce a splendid crystalline body. These new products were found to be comparable to the *iodide of ammonium*. The methyl compound for instance may be viewed as iodide of ammonium modified by the substitution of methyl for hydrogen. We may thus indicate the relationship of the two bodies:



When strongly heated the iodide of tetramethyl-ammonium splits up into the very products from which it was prepared, namely, trimethylamine and iodide of methyl.

We have seen that methyl can be introduced into rosaniline by three separate displacements of hydrogen. An interesting question now arises: Will trimethyl-rosaniline combine, like trimethylamine, with iodide of methyl? It will, and the product is a beautiful colouring matter. Recollecting that the development of a blue tint in the Hofmann violets indicated successive substitutions of methyl for hydrogen, we might reasonably conclude that this new methyl compound

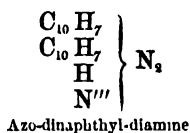
would be still bluer than a salt of trimethyl-rosaniline. The excess of methyl, however, gives us a colour which lies beyond pure blue, our complex product being the important blue-green colouring matter known as the "Iodine Green." It is now extensively used for dyeing cotton and silk, and owing to its strong blue tinge it gives a great variety of shades when employed in combination with yellow. This green product when strongly heated splits up into the compounds from which it was formed, namely, trimethyl-rosaniline and iodide of methyl.

There is still another aniline green which is now very extensively employed for calico printing. It is a feeble organic base producing crystalline salts, but its chemical relations have not been fully studied. It is known commercially as "Perkin's Green."

I must now call your attention to a red colouring matter, which, like the mauve, is a product of the oxidation of aniline. Its shade of colour approximates to that of "safflower extract," the colouring matter of the *Carthamus tinctorius*, and is much redder than magenta. I first obtained this product several years ago, but only in small quantities. Improved methods for preparing it have been proposed, and it is already employed to a limited extent in the arts. It is commonly called "Aniline Pink." It is also known as "Safranine," but this name properly belongs to the colouring matter of saffron. I am at present engaged in an investigation of the chemical nature of this body, and from the results already obtained, I conclude that it contains an organic base which gives crimson solutions with acids and forms crystallizable salts. This base appears to be composed of $C_{18}H_{18}N_2$, and its reactions show that it is closely related to mauveine.

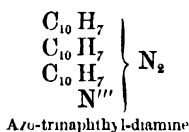
Last year, M. Clavel, of Basle, patented a process for producing a new colouring matter from *naphthalin*, or rather from *naphthylamine*, or, according to his own statement, from "an isomer of naphthylamine." This process consists in heating together equal quantities of the "isomeric naphthylamine," acetic acid, and nitrite of potassium to about $120^{\circ}C.$, and then adding naphthylamine, the temperature being maintained at $120^{\circ}C.$ until the desired colour is produced. When purified, the product is a beautiful crimson colour, specially adapted for silk dyeing.

Several years ago, Mr. Church and myself obtained by the action of nitrites on salts of naphthylamine a beautiful crystalline compound, called *azo-dinaphthyl-diamine*, consisting of two molecules of naphthylamine linked together by an atom of trivalent nitrogen occupying the place of three atoms of hydrogen. Its formula may be written thus :



This substance is an organic base, giving a solution of an orange-

yellow colour, and producing with acids various salts, some of which are violet. Now I find that M. Clavel's new colouring matter can readily be produced from this azo-dinaphthyl-diamine by a process which appears to elucidate its chemical nature without compelling us to assume the existence of an isomeric naphthylamine. On heating azo-dinaphthyl-diamine with *ordinary* naphthylamine and an acid, we obtain the new product by a reaction which seems to be analogous to that which occurs when rosaniline is boiled with aniline. In the latter case we know that phenyl is substituted for hydrogen, and there can be little doubt that the reaction we are now considering consists in the substitution of naphthyl for hydrogen, the product being *azo-trinaphthyl-diamine*, which may be thus formulated :



This new dye is known in commerce as "Magdala." On boiling our azo dinaphthyl-diamine with aniline we obtain another red colouring matter which is probably *azo-phenyl dinaphthyl-diamine*.

The aniline pink and the magdala are characterized by a remarkable fluorescence in the green rays of the spectrum.

The last result obtained in the production of colouring matters indicates a perfectly new line of research. Nearly all the coal-tar colours contain organic bases which may be viewed as representatives of ammonia, but the discovery referred to directs our attention to products of a different class—products which do not contain nitrogen. This discovery derives additional importance from the fact that it is a precedent for the artificial production of the natural colouring matters. The product recently obtained is in fact the true colouring matter of the madder root, namely "Alizarine."

Graebe and Liebermann found that nascent hydrogen converted natural alizarine into a hydro-carbon, which proved to be *anthracene*, one of the coal-tar products. This result naturally suggested an attempt to produce alizarine from anthracene by working backwards, and the well-directed labours of the two chemists have been crowned with success. Several years since, Dr. Anderson obtained an oxygenated derivative of anthracene, having the composition $\text{C}_{14} \text{H}_8 \text{O}_2$, and now called *anthraquinone*. On treating this with bromine, Graebe and Liebermann obtained *bibromo-anthraquinone*, having the formula $\text{C}_{14} (\text{H}_6 \text{Br}_2) \text{O}_2$, and this compound, when digested with potash, gave them alizarine, which has the formula $\text{C}_{14} \text{H}_8 \text{O}_4$. I may remind you that alizarine is one of our most important colouring matters, being extensively used for the production of Turkey red, and our lilac, pink, and chocolate prints.

I have given you a brief history of the principal artificial colouring matters, and have endeavoured to elucidate the constitution or

structure of those which have been studied by chemists. Though the beautiful relations of rosaniline and its derivatives are now very evident, it must be admitted that for want of sufficient data we are compelled to regard many of our colouring matters as isolated products. We may, however, detect some slight connecting threads of chemical relationship between all the coal-tar colours. They may be said to have a common origin, as they can be generally described as phenylic derivatives. The hydro-carbons from which most of them are produced contain the radical phenyl; thus benzol is the hydride of phenyl, while toluol may be regarded as a compound of phenyl and methyl. We do not find, however, that these and other substances containing phenyl are colouring matters, but the development of colour seems to attend the removal of hydrogen from phenyl. Thus in rosaniline and mauveine we appear to have the radical *phenylene* C_6H_5 , which is simply phenyl deprived of an atom of hydrogen. I do not assert that this particular radical is common to all the colour-producing bases, but I have come to the conclusion that each of these bases contains a phenyl residue, that is to say, phenyl more or less dehydrogenated. The natural colouring matters have been only partially studied, but some of them undoubtedly contain phenyl residues. We thus trace a connection between the colours produced artificially and those formed in the laboratory of nature.

When I commenced my lecture, I referred to the rapid advances of applied science. The history of the production of artificial colouring matters is a striking illustration of scientific progress. The new industry which emerged from the laboratory only thirteen years ago has attained such vast proportions, that its present annual value is computed to be more than a million and a quarter. Now that we are beginning to produce the natural colouring matters from coal-tar, it is impossible to form any conception of the ultimate magnitude of this important industry. .

[W. H. P.]

Friday, June 4, 1869.

His Royal Highness the PRINCE OF WALES, K.G. Vice-Patron,
in the Chair.

WILLIAM ODLING, Esq. M.B. F.R.S.

EULFRIAN PROFESSOR OF CHEMISTRY, R.I.

On the Simplest Organic Compounds.

ALL the olefine hydrocarbons are found to have one and the same ultimate composition, or ratio of carbon to hydrogen.

$C_2 H_4$	Ethylene
$C_3 H_6$	Propylene
$C_4 H_8$	Butylene
$C_5 H_{10}$	Amylene
$C_x H_{2x}$	&c., &c.

But these hydrocarbons obviously differ in the complexity of their constitution. Some of them are gases, differing from one another in condensability; others of them are liquids, differing from one another in volatility; while others of them are solids, differing from one another in fusibility. The exact degree of complexity of each hydrocarbon is shown by its reactions. Thus the hydrogen of gaseous ethylene being experimentally divisible into four parts, and its carbon into two parts, there is deduced for it the formula $C_2 H_4$; while the hydrogen of liquid amylene being experimentally divisible into ten parts, and its carbon into five parts, there is deduced for it the formula $C_5 H_{10}$. Again, it is possible to extract from a given volume of ethylene gas and amylene vapour, four times and ten times respectively the actual weight of hydrogen obtainable from the same volume of hydrochloric acid gas; and also to extract therefrom two times and five times respectively the actual weight of carbon that is obtainable from the same volume of carbonic acid gas—these two gases, formulated as HCl and CO_2 , containing within a given volume the smallest observed weights of hydrogen and of carbon respectively. The olefine hydrocarbons are said to be polymeric, and their different properties are satisfactorily referable to the different relative weights of their units or molecules. There exist many other series of polymeric bodies, that is of bodies having one and the same ultimate composition, but different molecular weights.

II.

Acetone, propion-aldehyd, and allyl-alcohol are entirely different substances, possessed of well-marked distinctive properties. Like the several olefines, they have the same ultimate composition as each other; but, unlike the several olefines, they have also the same molecular weight as each other, and are expressed by the same molecular formula C_3H_6O . In each of them the carbon is experimentally divisible into three parts, and the hydrogen into six parts, while the oxygen is indivisible; and it is possible to extract from any given volume of one of them exactly the same weights of carbon, hydrogen, and oxygen that are obtainable from the same gas-volume of each of the other two. These different bodies are said to be metameric, and their different properties are necessarily referable to a difference in the arrangement of their constituent elements.

III.

The existence of a determinate structural arrangement in chemical compounds is further demonstrated by a host of considerations; but the difficulty of making out the actual structure of individual compounds has hitherto proved insuperable. The facility of setting forth imaginary structure, however, is very great; and accordingly the presentation of imaginary for ascertained structure has been freely practised by chemists from the first introduction of chemical formulæ until now. But in what degree soever a determination of absolute chemical structure may hereafter be achieved, the possibility exists very generally, even at the present day, of determining relative chemical structure—of making out that in such and such a body the structural arrangement is similar to, or different from, that of some other and usually more simple body. Hence the importance of studying the structural analogies of the simplest organic bodies.

IV.

Marsh-gas is furnished by the decay of moist vegetable tissue, and in other ways. Chloride of methyl-gas is furnished by the action of hydrochloric acid upon narcotine, codeine, wood-spirit, &c. The ultimate composition of the two gases is expressed by the formulæ CH_4 and CH_3Cl respectively. Marsh-gas is transformable into methyl-chloride by the action of chlorine; and methyl-chloride into marsh-gas by the action of hydrogen. From this mutual metamorphosis, and from the parallelism of their properties, formations, and transformations, the two gases are inferred to have one and the same molecular structure, whatever that may be; and the same conclusion is applicable to the entire series of bodies formulated below:—

CH_4	Marsh-gas.
CH_3Cl	Methyl-chloride.
CH_2Cl_2	Methylen-dichloride.
$CHCl_3$	Chloroform.
CCl_4	Perchloride of carbon.

V.

Wood-spirit is usually furnished by the destructive distillation of wood, but is procurable from many other sources, and especially from essential oil of winter-green, by its decomposition with potash. The ultimate composition of wood-spirit is expressed by the formula CH_3O ; and it is observable that the difference of ultimate composition between wood-spirit and methyl-chloride CH_3Cl , is the same as that between water H_2O , and hydrochloric acid HCl ; as is shown more clearly by the following formulæ, in which the differential constituents of the two pairs of bodies are included in parentheses.



Further, the residue H of hydrochloric acid and residue CH_3 of methyl-chloride are transformable into water and wood-spirit respectively, and re-transformable from water and wood-spirit back to hydrochloric acid and methyl-chloride respectively, by precisely similar reactions.

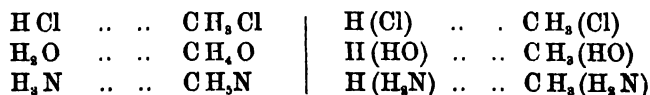
From the mutual metamorphoses and parallel habitudes of the two bodies, methyl-chloride and wood-spirit, it is inferred that, with regard to their common residue CH_3 , they have the same structure as one another; while, with regard to their differential constituents, (Cl) and (HO) , their difference of structure is analogous to the difference between hydrochloric acid and water.

VI.

Hydrochloric acid HCl , and water H_2O , are the first and second terms of a series of bodies of which the third and fourth terms are constituted by ammonia H_3N , and marsh-gas H_4C respectively. Hence arises a question as to the existence of organic bodies bearing to methyl-chloride and wood-spirit the relation that ammonia and marsh-gas bear to hydrochloric acid and water.

VII.

Many years ago, methyl-amine was discovered by Wurtz. It is now known to occur as a product of the putrefaction of, and also of the action of alkalis upon, many animal substances. Its resemblance in properties to ammonia is most remarkable, and its differentiation therefrom somewhat difficult. Its ultimate composition is expressed by the formula CH_3N ; whence it appears that the difference of ultimate composition between methyl-amine and wood-spirit and methyl-chloride is the same as that between ammonia and water and hydrochloric acid.

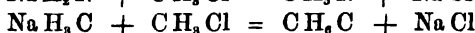
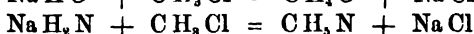
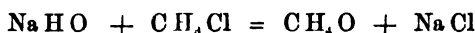


Moreover, methyl-amine, wood-spirit, and methyl-chloride are mutually convertible, through exchanges of their differential consti-

tments, by processes effecting similar mutual conversions of hydrochloric acid, water, and ammonia. From the mutual metamorphoses and parallel habitudes of the three bodies, it is inferred that, with regard to their common residue CH_3 , they have the same structure as each other, while with regard to their differential constituents (Cl), (HO), and (H_2N), their difference of structure is similar to the difference between hydrochloric acid and water and ammonia.

VIII.

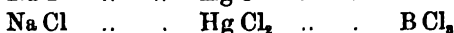
Wood-spirit or methyl-hydrate is producible by the action of methyl-chloride upon sodium-hydrate NaHO ; and methyl-amine by the action of methyl-chloride upon sodium-amide NaH_2N . Similarly, methyl-methide is producible by the action of methyl-chloride upon sodium-methide NaH_3C . (Action of methyl-iodide upon zinc-methide.—Frankland and Kolbe.)



This methyl-methide is now known to be identical with the hydrocarbon C_2H_6 , producible by the indirect deoxidation of common alcohol $\text{C}_2\text{H}_5\text{O}$, and known as ethane or hydride of ethyl. Ethane $\text{CH}_3(\text{H}_3\text{C})$, being susceptible of two distinct and similar sets of marsh-gas reactions, just as methyl-amine $\text{CH}_3(\text{H}_2\text{N})$ is susceptible of one set of marsh-gas and one set of ammonia reactions—as before, an identity of structure between ethane and methyl-amine is inferred with respect to their common residue CH_3 , and a difference of structure with respect to their differential constituents (H_3C) and (H_2N), parallel to the difference in structure between marsh-gas and ammonia.

IX.

The property of oxygen that is half-saturated by hydrogen, or of the water residue HO'' , and the property of nitrogen that is two-thirds saturated by hydrogen, or of the ammonia residue $\text{H}_2\text{N}'''$, to suffer an exchange for one proportion of chlorine or hydrogen, has been shown in the above, and might be shown in many other compounds. But oxygen, altogether unsaturated by hydrogen, has the additional property of being exchangeable for two proportions of chlorine or hydrogen; and nitrogen, altogether unsaturated by hydrogen, has the additional property of being exchangeable for three proportions of chlorine or hydrogen, as indicated by the succeeding formulæ for mercuric oxide and mercuric chloride, and for boric nitride and boric chloride respectively.



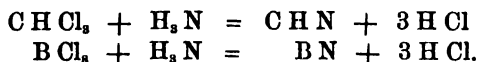
Marsh-gas compounds, in which hydrogen or chlorine has been exchanged for half-saturated oxygen and two-thirds saturated nitrogen, have been already adduced in wood-spirit CH_4O , and methylamine CH_3N ; and reference has also been made to the corresponding hydro-carbon CH_4C or C_2H_2 . The question now arises as to the existence of marsh-gas compounds in which hydrogen or chlorine has been exchanged for else unsaturated oxygen and nitrogen, and of hydrocarbons corresponding to these compounds.

X.

Some few years back a curious oxidation product of wood-spirit was discovered by Hofmann. It is now called formic aldehyd, and its ultimate composition is expressed by the formula CH_2O . In respect of ultimate composition its relationship to the second marsh-gas chloride CH_2Cl_2 is obviously similar to that of mercuric oxide HgO , to mercuric chloride HgCl_2 . Both formic aldehyd and methylen dichloride, however, are imperfectly studied compounds, and their actual metamorphoses are unknown. But in the case of many other aldehyds and corresponding organic dichlorides, the relationship of mutual metamorphosis is well established, whence it is believed to exist between these two compounds also. On this assumption formic aldehyd $\text{CH}_2\text{O}''$, and methylen dichloride CH_2Cl_2 , are inferred to have one and the same structural arrangement in respect to their common residue CH_2 , and a difference of structure in respect to their differential constituents O'' and Cl_2 , similar to the difference between oxide and chloride of mercury for example.

XI.

Prussic acid is a well-known organic compound producible by the action of water on bitter almond kernels, and in various other ways. Its ultimate composition being expressed by the formula CHN , the difference in ultimate composition between it and chloroform CHCl_3 , is obviously similar to the difference in composition between nitride and chloride of boron, BN and BCl_3 , respectively. Now chloroform is readily converted into prussic acid, and boric chloride into boric nitride, by the similar action of ammonia upon the two compounds, with exchange of Cl_3 for N''' , thus:—



Prussic acid CHN''' , and chloroform CHCl_3 , are accordingly inferred to have one and the same structure in respect of their common residue CH , and a difference of structure in respect of their differential constituents N''' and Cl_3 , parallel to the difference between nitride and chloride of boron for example.

XII.

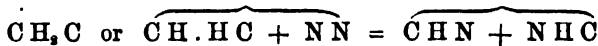
Allowing for the different replaceable values of oxygen O'', and nitrogen N''', the relationship of methyl-amine to prussic acid is comparable with that of formic aldehyd to wood-spirit:—

Wood-spirit	$\text{C H}_4 \text{O}$	Formic aldehyd	$\text{C H}_2 \text{O}$	
Methylamine	$\text{C H}_5 \text{N}$		"	Prussic acid C H N
Ethane	$\text{C H}_6 \text{C}$	Ethylene	$\text{C H}_4 \text{C}$	Acetylene $\text{C H}_2 \text{C}$

Prussic acid and formic aldehyd are procurable from methylamine and wood-spirit respectively, by similar processes of dehydrogenation or oxidation; while methyl-amine actually, and wood-spirit analogically, are reproducible from prussic acid and formic aldehyd by the reverse process of hydrogenation. Now the difference in ultimate composition, between ethane and olefant gas, or ethylene, is similar to that between wood-spirit and formic aldehyd; and the difference of ultimate composition, between the hydrocarbons ethane and acetylene, is similar to that between methyl-amine and prussic acid. Moreover ethane is convertible successively into ethylene and acetylene by oxidation; and acetylene is reconvertible into ethylene and ethane successively by hydrogenation.

XIII.

The experimental relationship of ethane, methyl-amine, and wood-spirit has been already considered. Formic aldehyd being a very imperfectly-studied compound, the relationship between it and ethylene is as yet analogical only; but the experimental relationship between acetylene and prussic acid has recently been established by Berthelot, who has shown that mixed acetylene and nitrogen are convertible into prussic acid, and that prussic acid is reconvertible into mixed acetylene and nitrogen, by the action of the electric spark.



XIV.

Just as the existence in methyl-chloride, in formic aldehyd, and in prussic acid of one marsh-gas residue, plus one hydrochloric acid residue Cl', and one water residue O'', and one ammonia residue N''', respectively, is inferable from the relationships and behaviour of the respective bodies—so is the existence alike in ethane, ethylene, and acetylene of two marsh-gas residues inferable from the relationships and behaviour of these respective bodies. As shown more especially by Kekulé, the individual marsh-gas residues of every hydrocarbon are found to be susceptible of changes exactly similar to those of marsh-gas itself, and resulting in the formation of similarly characterized bodies, as indicated below in the case of some ethane and ethylene derivatives.

Ethyl chloride	$C_2H_5 \cdot C_2H_5 (Cl)$	Vinyl-chloride	$C_2H_5 \cdot CH (Cl)$
Alcohol . .	$C_2H_5 \cdot C_2H_5 (HO)$	Vinyl-alcohol	$C_2H_5 \cdot CH (HO)$
Ethylamine	$C_2H_5 \cdot C_2H_5 (H_2N)$	Vinyl-amine	$C_2H_5 \cdot CH (H_2N)$
Propane . .	$C_2H_5 \cdot C_2H_5 (H_3C)$	Propylene	$C_2H_5 \cdot CH (H_3C)$

XV.

In any hydrocarbon or chlorhydrocarbon, the substitution of half-saturated oxygen HO'' , for one proportion of hydrogen or chlorine, is productive of a compound either similar or dissimilar in its properties to common alcohol C_2H_5O or $CH_3 \cdot CH_2(HO)$. Hence, from an examination of the resulting product, and of its other modes of formation, an inference is deducible as to its genesis having resulted from a change effected in the marsh-gas residue CH_3 in the former case, and from a change effected in one or other of the marsh-gas residues CH_2 and CH in the latter case.

In any hydrocarbon or chlorhydrocarbon, the substitution of one proportion of oxygen O'' , for two proportions of hydrogen or chlorine, is productive of a compound either similar or dissimilar in its properties to common aldehyd C_2H_4O or $CH_3 \cdot CHO''$. Hence, from an examination of the resulting product, and of its other modes of formation, an inference is deducible as to its genesis having resulted from a change effected in the marsh-gas residue CH_3 in the former case, and from a change effected in the marsh-gas residue CH_2 in the latter case.

The relative structure of the previously cited metameric compounds propion-aldehyd, acetone, and allyl-alcohol is thus ascertainable, and is expressed in the following structural formulæ:—

Hydrocarbon.	Metameric Derivatives.
C_3H_8 or $CH_3 \cdot CH_2 \cdot CH_3$	$\begin{cases} CH_3 \cdot CH_2 \cdot CHO'' & \text{Propion-aldehyd.} \\ CH_3 \cdot CO \cdot CH_3 & \text{Acetone.} \end{cases}$
C_3H_6 or $CH_2 \cdot CH \cdot CH_3$	$CH_2 \cdot CH \cdot CH_2(HO)$ Allyl-alcohol.

[W. O.]

Friday, January 28, 1870.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, M.B. F.R.S.

FULFILLING PROFESSOR OF CHEMISTRY, &c.

On Professor Graham's Scientific Work.

THE simple story of Mr. Graham's life, though not without its measure of interest, and certainly not without its lessons, is referred to in the following pages only in illustration of the grander story of his work. Thomas Graham was born in Glasgow, on the 21st Dec., 1805. He entered as a student at the University of Glasgow, in 1819, with a view to becoming ultimately a Minister of the Established Church of Scotland. At that time, the University chair of Chemistry was filled by Dr. Thomas Thomson, a man of very considerable mark, and one of the most erudite and thoughtful chemists of his day. The chair of Natural Philosophy was also filled by a man of much learning, Dr. Meikleham, who appears to have taken a warm personal interest in the progress of his since distinguished pupil. Under these masters, Mr. Graham acquired a strong liking for experimental science, and a dislike to the profession chosen for him by his father; who, for a time at least, seems to have exerted the authority of a parent somewhat harshly, but quite unavailingly, to effect the fulfilment of his own earnest wishes in the matter.

After taking his degree of Master of Arts at Glasgow, in 1826, Mr. Graham worked for nearly two years in the laboratory of the University of Edinburgh, under Dr. Hope. He then returned to Glasgow; and, while supporting himself by teaching, at first mathematics and afterwards chemistry, yet found time to follow up the path of experimental inquiry, on which he had already entered.

His first original paper appeared in the 'Annals of Philosophy' for 1826, its author being at that time in his twenty-first year. It is interesting to note that the subject of this communication, "On the Absorption of Gases by Liquids," forms part and parcel of that large subject of spontaneous gas-movement with which Mr. Graham's name is now so inseparably associated; and that, in a paper communicated to the Royal Society just forty years later, he speaks of the lique-

fiability of gases by chemical means, in language almost identical with that used in this earliest of his published memoirs.

Having, in the interval, contributed several other papers to the scientific journals, in the year 1829 he published in the 'Quarterly Journal of Science'—the journal, that is to say, of the Royal Institution—the first of his papers relating specifically to the subject of gas-diffusion. It was entitled "A short Account of Experimental Researches on the Diffusion of Gases through each other, and their Separation by Mechanical Means." In the same year, he became Lecturer on Chemistry at the Mechanics' Institute, Glasgow; and in the next year, 1830, achieved the yet more decisive step of being appointed Professor of Chemistry at the Andersonian University. By this appointment he was relieved from anxiety on the score of living; and afforded, in a modest way, the means of carrying out his experimental work.

In 1831, he read, before the Royal Society of Edinburgh, a paper "On the Law of the Diffusion of Gases," for which the Keith prize of the Society was shortly afterwards awarded him. Although several of his earlier papers, and especially that on the Diffusion of Gases, published in the 'Quarterly Journal of Science,' had given evidence of considerable power, it was this paper—in which he established the now well-recognized law that the velocities of diffusion of different gases are inversely as the square roots of their specific gravities—that constituted the first of what may properly be considered his great contributions to the progress of chemical science.

In 1833, he communicated a paper, of scarcely less importance, to the Royal Society of London, entitled "Researches on the Arseniates, Phosphates, and Modifications of Phosphoric Acid." It afforded further evidence of Mr. Graham's quiet steady power of investigating phenomena, and of his skill in interpreting results; or rather of his skill in setting forth the results in all their simplicity, undistorted by the gloss of preconceived notions, so as to make them render up their own interpretation. It is difficult now-a-days to realize the independence of mind involved in Mr. Graham's simple interpretation of the facts, presented to him in this research, by the light of the facts themselves, irrespective of all traditional modes of viewing them. Their investigation let in a flood of light upon the chemistry of that day; and formed a starting-point from which many of our most recent advances may be directly traced. In this paper, Mr. Graham established the existence of two new, and, at that time, wholly unanticipated classes of bodies, namely, the class of polybasic acids and salts, and the class of so-called anhydro-acids and salts. The views of Graham on the polybasicity of phosphoric acid were soon afterwards applied by Liebig to tartaric acid, and by Gerhardt to polybasic acids in general, as we now recognize them. After a long interval, the idea of polybasicity was next extended to radicals and to metals by Williamson and myself successively; afterwards to alcohols by Wurtz, and to ammonias by Hofmann. The

notion of anhydro-salts was extended by myself to the different classes of silicates; by Wurtz to the compounds intermediate between oxide of ethylene and glycol; and by other chemists to many different series of organic bodies.

The next most important of the researches, completed by Mr. Graham while at Glasgow, was the subject of a paper communicated to the Royal Society of Edinburgh, in 1835, "On Water as a Constituent of Salts," and of a second paper communicated to the Royal Society of London, in 1836, entitled "Inquiries respecting the Constitution of Salts, &c.," for which latter, a Royal medal of the Society was afterwards awarded. The subject of hydration had yielded him such a harvest of results in the case of phosphoric acid, that it was only natural he should wish to pursue the inquiry farther. Indeed, it is a curious illustration of the persistency of the man, that he never seems to have left out of sight the subjects of his early labours. Almost all his subsequent original work is but a development, in different directions, of his youthful researches on gas-diffusion and water of hydration; and so completely did he bridge over the space intervening between these widely remote subjects, that, with regard to several of his later investigations, it is difficult to say whether they are most directly traceable to his primitive work on the one subject or on the other.

In 1837, on the death of Dr. Edward Turner, Mr. Graham was appointed Professor of Chemistry at University College, London, then called the University of London. On his acceptance of this appointment, he began the publication of his well-known 'Elements of Chemistry,' which appeared in parts, at irregular intervals, between 1837 and 1841. Elementary works, written for the use of students, have necessarily much in common; but the treatise of Mr. Graham, while giving an admirably digested account of the most important individual substances, was specially distinguished by the character of the introductory chapters, devoted to Chemical Physics; wherein was set forth one of the most original and masterly statements of the first principles of chemistry that has ever been placed before the English student. "The Theory of the Voltaic Circle" had formed the subject of a paper communicated by Mr. Graham to the British Association in 1839; and the account of the working of the battery, given in his Elements of Chemistry, and based on the above paper, will long be regarded as a model of lucid scientific exposition.

In 1841, the now flourishing Chemical Society of London was founded; and though Mr. Graham had been, at that time, but four years in London, such was the estimation in which he was held by his brother chemists, that he was unanimously chosen as the first President of the Society. The year 1844 is noticeable in another way. Wollaston and Davy had been dead for some years. Faraday's attention had been diverted from chemistry to those other branches of experimental inquiry in which his highest distinctions were achieved; and, by the death of Dalton in this year, Mr. Graham was left as the acknowledged

first of English chemists, as the not unworthy successor to the position of Black, Priestley, Cavendish, Wollaston, Davy, and Dalton.

From the period of his appointment at University College, in 1837, Mr. Graham's time was fully occupied in teaching, in writing, in advising on chemical manufactures, in investigating fiscal and other questions for the Government, and in the publication of various scientific memoirs, several of them possessing a high degree of interest; but it was not till 1846 that he produced a research of any considerable magnitude. In that year he presented to the Royal Society the first part of a paper "On the Motion of Gases," the second part of which he supplied in 1849. For this research, Mr. Graham was awarded a second Royal Medal of the Society in 1850. The preliminary portion of the first part of the paper related to an experimental demonstration of the law of the effusion of gases, deduced from Torricelli's theorem on the efflux of liquids,—a demonstration that was achieved by Mr. Graham with much ingenuity, and without his encountering any formidable difficulty. But the greater portion of the first part, and whole of the second part, of this most laborious paper, were devoted to an investigation of the velocities of transpiration of different gases through capillary tubes; with a view to discover some general law by which their observed transpiration rates might be associated with one another. Again and again, with characteristic pertinacity, Mr. Graham returned to the investigation; but, although much valuable information of an entirely novel character was acquired—information having an important bearing on his subsequent work—the problem itself remained, and yet remains, unsolved. Why, for example, under an equal pressure, oxygen gas should pass through a capillary tube at a slower rate than any other gas is a matter that still awaits interpretation.

Near the end of the same year, 1849, Mr. Graham communicated, also to the Royal Society, a second less laborious, but in the novelty and interest of its results more successful, paper "On the Diffusion of Liquids." It was made the Bakerian lecture for 1850; and was supplemented by further observations communicated to the Society in 1850 and 1851. In his investigation of this subject, Mr. Graham applied to liquids the exact method of inquiry which he had applied to gases just twenty years before, in that earliest of his papers on the subject of gas-diffusion published in the 'Quarterly Journal of Science;' and he succeeded in placing the subject of liquid-diffusion on about the same footing as that to which he had raised the subject of gas-diffusion prior to the discovery of his numerical law.

In 1854, Mr. Graham communicated another paper to the Royal Society, "On Osmotic Force," a subject intimately connected with that of his last previous communication. This paper was also made the Bakerian lecture for the year; but, altogether, the conclusions arrived at were hardly in proportion to the very great labour expended on the inquiry. In the next year, 1855, just five-and-twenty years after his appointment at the Andersonian University, Mr. Graham was

made Master of the Mint; and, as a consequence, resigned his Professorship at University College. During the next five years he published no original work.

Thus, at the beginning of the year 1861, Mr. Graham, then fifty-six years of age, had produced, in addition to many less important communications, five principal memoirs; three of them in the highest degree successful; the other two less successful in proportion to the expenditure of time and labour on them, but, nevertheless, of great originality and value. The most brilliant period, however, of his scientific career was to come. In the year 1861, and between then and his death in 1869, Mr. Graham communicated four elaborate papers to the Royal Society; three of them far exceeding in novelty, interest, and philosophic power anything that he had before produced; and the other of them, relating to a certain physical effect of that hydration of compounds, from the consideration of which his attention could never wholly be withdrawn. This least important paper, "On Liquid Transpiration in relation to Chemical Composition," was communicated to the Royal Society in 1861. Of the three greater papers, that "On Liquid Diffusion applied to Analysis" was communicated also in 1861. For this paper more especially, as well as for his Bakerian lectures "On the Diffusion of Liquids" and "On Osmotic Force," Mr. Graham received, in 1862, the Copley Medal of the Royal Society; and, in the same year, was also awarded the Jecker Prize of the Institute of France. Following in quick succession, his paper "On the Molecular Mobility of Gases" was presented to the Royal Society in 1863; and that "On the Absorption and Dialytic Separation of Gases by Colloid Septa," in 1866. With regard to these three great papers, two of them were each supplemented by a communication to the Chemical Society; while the third was supplemented by four successive notes to the Royal Society, containing an account of further discoveries on the same subject, hardly less remarkable than those recorded in the original paper. The last of these supplementary notes was communicated on June 10th, 1869, but a few months before the death, on September 13th, of the indefatigable but physically broken-down man.

In considering Mr. Graham as a chemical philosopher and law-giver we find him characterized by a pertinacity of purpose peculiarly his own. Wanting the more striking qualities by which his immediate predecessors, Davy, Dalton, and Faraday, were severally distinguished, he displayed a positive zeal for tedious quantitative work, and a wonderful keen-sightedness in seizing the points which his innumerable determinations of various kinds, conducted almost incessantly for a period of forty years, successively unfolded. His work itself was essentially that of detail, original in conception, simple in execution, laborious by its quantity, and brilliant in the marvellous results to which it led. As regards its simplicity of execution, scarcely any investigator of recent times has been less a friend to the instrument-maker than Mr. Graham. While availing himself,

with much advantage, of appliances devised by Bunsen, Poiseuille, Sprengel, and others, all the apparatus introduced by himself was of the simplest character, and for the most part of laboratory construction.

Essentially inductive in his mode of thought, Mr. Graham developed his leading ideas, one after another, directly from experiment, scarcely, if at all, from the prevailing ideas of the time. As well observed by Dr. Angus Smith, "he seemed to feel his way by his work." His records of work are usually, in a manner almost characteristic, preceded each by a statement of the interpretation or conclusion which he formed; but the records themselves are expressed in the most unbiassed matter-of-fact language. Singularly cautious in drawing his conclusions, he announces them from the first with boldness, making no attempt to convince, but leaving the reader to adopt them or not as he pleases. Accordingly, in giving an account of his various researches, Mr. Graham rarely, if ever, deals with argument; but he states succinctly the experiments he has made, the conclusions he has himself drawn, and not unfrequently the almost daring speculations and generalizations on which he has ventured. Some of these speculations, on the constitution of matter, are reproduced in his own words farther on.

Mr. Graham was elected a Fellow of the Royal Society in 1837; Corresponding Member of the Institute of France in 1847; and Doctor of Civil Law of Oxford in 1855.

The remaining pages of this abstract are devoted to an account of his principal discoveries,—the generalizations they suggested to him, and the relations in which they stood to precedent knowledge.

I.

Modifications of Phosphoric Acid.—At the date of Mr. Graham's investigation of this subject, when oxy-salts were usually represented as compounds of anhydrous base with anhydrous acid, the point of greatest importance, with regard to each class of salts, was held to be the ratio borne by the oxygen of the base to the oxygen of the acid. Thus, in the carbonates, this ratio was as 1 to 2; in the sulphates, as 1 to 3; and in the nitrates, as 1 to 5. But with regard to the phosphates, taking common phosphate of soda as a type of phosphates in general, there was a difficulty. Dr. Thomson maintained that, in this salt, the ratio of the oxygen of the base to the oxygen of the acid was as 1 to 2; and his view was substantially supported by Sir Humphry Davy. Berzelius contended, however, that the ratio was as 1 to $2\frac{1}{2}$, or, to avoid the use of fractions, as 2 to 5; but, notwithstanding the excellence of the Swedish chemist's proof, and its corroboration by the researches of others, the simpler and, as it seemed, more harmonious view of Dr. Thomson prevailed very generally in this country. Anyhow, those phosphates in which the oxygen ratio was the same as that in phosphate of soda were taken as the neutral

salts. But phosphate of soda was found to have the peculiar and quite inexplicable property of reacting with nitrate of silver to throw down, as a yellow precipitate, a phosphate of silver, in which the proportion of metallic base exceeded that in the original phosphate of soda,—the precipitation of the basic salt being accompanied correlatively by the formation of a strongly acid liquid. According to Berzelius, the ratio of the oxygen of the base to that of the acid, in this yellow precipitate, was as 3 to 5.

In 1821, Mitscherlich, then working in Berzelius's laboratory, obtained, by treating ordinary phosphate of soda with aqueous phosphoric acid, a new crystallizable phosphate of soda, in which the ratio of acid to base was twice as great as that in the ordinary phosphate. This new salt, which had a strongly acid reaction to test paper, he called the bi-phosphate of soda. He observed that it was a hydrated salt; and that while the ratio, in it, of the oxygen of the base to the oxygen of the acid was as 1 to 5, the ratio of the oxygen of the base to the oxygen of the water was as 1 to 2.

In 1827, Mr. Graham's fellow-townsmen, and predecessor at the Mechanics' Institute, Dr. Clark, discovered another new phosphate of soda, in which the ratio of the oxygen of the base to the oxygen of the acid was identical with that in the ordinary phosphate, namely, as 2 to 5. But whereas the ordinary phosphate crystallized with 25 proportions of water, the new phosphate crystallized with only 10; and whereas the ordinary phosphate gave a yellow precipitate with nitrate of silver and a strongly acid supernatant liquid, the new phosphate gave a chalk-white precipitate with nitrate of silver and a perfectly neutral supernatant liquid. This new phosphate, being formed by heating the common phosphate to redness, was accordingly designated the pyrophosphate. By dissolution in water and evaporation of the liquid, it could be obtained in the 10-hydrated crystalline state; and by desiccation at a sand-bath heat, the crystalline salt could be again rendered anhydrous. With regard to the 25 proportions of water belonging to the ordinary salt, Dr. Clark noticed that 24 proportions could be driven off by a sand-bath heat, and that this moderate heat did not alter the nature of the salt. He found that the 25th proportion of water, however, could only be driven off by a full red heat; and that, simultaneously with its expulsion, the change in the nature of the salt was effected. But he carefully guarded himself against being supposed to think that the change in properties of the salt was consequent upon an elimination of its water. The driving off of water from salts being, as he justly remarked, a common effect of heat, he regarded this effect as a concomitant only of the peculiar effect of heat in altering the nature of the phosphate.

Other anomalies with regard to phosphoric acid and the phosphates were also known to chemists; and, on referring now to standard chemical works written before the year 1833, the whole subject of the phosphates will be seen to be in the greatest confusion. It was in this year that Mr. Graham communicated his paper, entitled "Researches

on the Arseniates, Phosphates, and Modifications of Phosphoric Acid," to the Royal Society.*

In the course of these researches he established the existence of a class of soluble sub-phosphates analogous to the yellow insoluble phosphate of silver; and he showed, with great clearness, that in the three classes of phosphates, namely, the sub-phosphates, the common phosphates, and the bi-phosphates, the ratio borne to the oxygen of the acid by the other oxygen of the salt is the same, namely, as 3 to 5; only that, in the three classes of salts, the non-acid oxygen is divided between different proportions of metallic base and water, thus:

Sub-phosphate of soda	3 Na O.P.O_3 .
Common phosphate of soda	H O.2 Na O.P.O_3 .
Bi-phosphate of soda	2 H O.Na O.P.O_3 .

He further pointed out that, to these three series of salts, there corresponded a definite phosphate of water, or,

Hydrated phosphoric acid	3 H O.P.O_3 .
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Compounds of one and the same anhydrous acid with one and the same anhydrous base, in different proportions, had long been known; but it was thus that Mr. Graham first established the notion of polybasic compounds, - the notion of a class of hydrated acids having more than one proportion of water replaceable by metallic oxide, and that successively, so as to furnish more and more basic salts, all preserving, as we should now say, the same type.

Mr. Graham further showed that Dr. Clark's pyrophosphate of soda, like the common phosphate, yielded an acid-salt or bi-phosphate; and that these two compounds were related to a hydrated phosphoric acid, differing in composition and properties from the above-mentioned hydrate, and yielding, after neutralization with alkali, a white instead of a yellow precipitate with nitrate of silver. This series of compounds he expressed by the following formulæ:

Clark's pyrophosphate of soda	2 Na O.P.O_3 .
Acid or bi-pyrophosphate of soda	H O.Na O.P.O_3 .
Hydrated pyrophosphoric acid	2 H O.P.O_3 .

Lastly, Mr. Graham showed that when the bi-phosphate or bi-pyrophosphate of soda was ignited, there was left a new variety of phosphate, which he called the metaphosphate, having the same proportions of soda and anhydrous phosphoric acid as the original compound, but differing from it in several properties, more particularly in its inability to furnish any acid salt. From this new phosphate he obtained the corresponding hydrated acid, and found it to be identical with that variety of phosphoric acid then, and still, known as glacial phosphoric acid; which had previously been noticed to possess

* Phil. Trans., 1833, p. 253.

the distinctive property of causing a precipitate in solutions of albumen. This salt and acid he represented as follows:—

Metaphosphate of soda	Na O.P O_4 .
Metaphosphoric acid	H O.P O_4 .

Speaking of the acid obtainable from, and by its neutralization reconverted into, the phosphate, pyrophosphate, and metaphosphate of soda respectively, Mr. Graham remarked:—"The acid, when separated from the base, will possess and retain for some time the characters of its peculiar modification. . . . But I suspect that the modifications of phosphoric acid, when in what we would call a free state, are still in combination with their usual proportion of base, and that that base is water. Thus the three modifications of phosphoric evidence may be composed as follows:—

Phosphoric acid	3H O.P O_4 ,
Pyrophosphoric acid		2H O.P O_4 ,
Metaphosphoric acid		H O.P O_4 ;

or they are respectively a triphosphate, a biphosphate, and phosphate of water." These remarks he followed up by analytical evidence, showing the existence of the three hydrates, each in its isolated state.

Just as in his demonstration of the relationship to one another of sub-phosphate of soda, phosphate of soda, bi-phosphate of soda, and common phosphoric acid, Mr. Graham originated the notion of polybasic compounds, so, in his demonstration of the nature of the pyrophosphates and metaphosphates, as bodies differing from the normal compounds by an abstraction of water or metallic base, did he originate the notion of anhydro-compounds—so did he discover, for the first time, an instance of that relationship between bodies which is now known to prevail most extensively among products of organic as well as of mineral origin.

The different properties manifested by phosphoric acid, in its different reputedly isomeric states, having been shown by Mr. Graham to be dependent on a difference of hydration, that is to say on a difference of chemical composition, he was inclined to view the difference of properties observed in the case of other reputedly isomeric bodies as being also dependent on a difference of composition, the difference occasionally consisting in the presence of some minute disregarded impurity. Accordingly, he communicated to the Royal Society of Edinburgh in 1834,* a paper "On Phosphuretted Hydrogen," in which he showed that the spontaneously inflammable and non-spontaneously inflammable varieties of the gas "are not isomeric bodies, but that the peculiarities of the spontaneously inflammable species depend upon the presence of adventitious matter," removable in various ways,

* 'Edin. Roy. Soc. Trans,' xiii. 1836, p 88.

and existing but in very minute proportion.* He further showed that the vapour of some acid of nitrogen, apparently "nitrous acid, is capable of rendering phosphuretted hydrogen spontaneously inflammable when present to the extent of *one ten-thousandth part* of the volume of the gas." In connection with this research, may be mentioned Mr. Graham's earlier experiments on the influence of minute impurities in modifying the chemical behaviour of different substances. In some "Observations on the Oxidation of Phosphorus," published in the 'Quarterly Journal of Science,'† for 1829, he showed that the presence of $\frac{1}{450}$ of olefiant gas, and even $\frac{1}{4400}$, by volume, of turpentine vapour, in air under ordinary pressure, rendered it incapable of effecting the slow oxidation of phosphorus. He also observed and recorded the influence upon the oxidation of phosphorus of various additions of gas and vapour to air, under different circumstances of pressure and temperature.

II.

Hydration of Compounds.—In the earliest of Mr. Graham's published memoirs, that "On the Absorption of Gases by Liquids,"‡ he contended that the dissolution of gases in water, at any rate of the more soluble gases, is a chemical phenomenon, depending on their essential property of liquefiability being brought into play by their reaction with the solvent, that is to say by their hydration. The results of some further work on the same subject he published under the title of "Experiments on the Absorption of Vapours by Liquids."§

In 1827, he gave to the Royal Society of Edinburgh "An Account of the Formation of Alcoholates, definite Compounds of Salts and Alcohol analogous to the Hydrates."|| In this paper, after a description of some experiments on the desiccation of alcohol, he showed that anhydrous chloride of calcium, nitrate of lime, nitrate of magnesia, chloride of zinc, and chloride of manganese have the property of uniting with alcohol, as with water, to form definite compounds. The crystalline compound with chloride of zinc, for instance, containing 15 per cent. of alcohol, he represented by the formula $\text{ZnCl} \cdot 2\text{C}_2\text{H}_5\text{O}$; corresponding to the modern formula $\text{ZnCl}_2 \cdot 2\text{C}_2\text{H}_5\text{O}$.

In 1835, Mr. Graham communicated a paper, also to the Royal Society of Edinburgh, "On Water as a Constituent of Salts."¶ In this paper he showed more particularly that the so-called magnesium sulphates, crystallizing usually with 7, 6, or 5 proportions of water, gave up all but the last proportion of water at a moderate heat, but retained this last proportion with great tenacity. The comparatively stable mono-hydrated salts, — monohydrated sulphate of zinc, for

* It was afterwards isolated by P. Thenard.

† 'Quart. Journ. Sci.,' ii., 1829, p. 83.

‡ Thomson, 'Ann. Phil.,' xii., 1826, p. 69.

§ 'Edin. Journ. Sci.,' viii., 1828, p. 326.

|| 'Edin. Roy. Soc. Trans.,' xi., 1837, p. 175.

¶ Ibid., xiii., 1836, p. 297.

instance, $\text{ZnO} \cdot \text{SO}_3 \cdot \text{HO}$,—he regarded as the analogues of crystallizable sulphuric acid $\text{HO} \cdot \text{SO}_3 \cdot \text{HO}$. He showed further that the firmly-retained water of sulphate of zinc, for instance, differed from the firmly-retained water of phosphate of soda, in not being basic, or replaceable, that is to say, by metallic oxide. He conceived, however, that in the double sulphates, potassio-sulphate of zinc, for instance, $\text{ZnO} \cdot \text{SO}_3 \cdot \text{KO} \cdot \text{SO}_3$, the water of the compound, $\text{ZnO} \cdot \text{SO}_3 \cdot \text{HO}$, was replaced by alkali-sulphate, and he accordingly designated the water of this last, and of similar compounds, by the name of saline or constitutional water.

In the following year, 1836, Mr. Graham communicated to the Royal Society of London an elaborate paper, entitled "Inquiries respecting the Constitution of Salts, of Oxalates, Nitrates, Phosphates, Sulphates, and Chlorides."* In it are recorded careful analyses of very many salts, more particularly in respect to their water of hydration; with remarks upon the greater or less tenacity with which the water is retained in different instances. In this paper he put forward the notion that truly basic salts are nevertheless neutral in constitution; and that the excess of metallic base does not stand in the relation of a base to the anhydrous acid, but as a representative of the water of hydration of the neutral salt. He illustrated this position by a comparison of the definite hydrate of nitric acid with other hydrated nitrates, thus :

Hydrated nitric acid, sp. gr. 1.42	. .	$\text{HO} \cdot \text{NO}_3 \cdot 3 \text{HO}$
Hydrated nitrate of zinc	$\text{ZnO} \cdot \text{NO}_3 \cdot 3 \text{HO}$
Hydrated nitrate of copper	$\text{CuO} \cdot \text{NO}_3 \cdot 3 \text{HO}$
Basic nitrate of copper	$\text{HO} \cdot \text{NO}_3 \cdot 3 \text{CuO}$

He contended that, in the last cupric salt, it is the water and not the oxide of copper which acts as a base; and, in support of this view, he remarked that if the water of the salt were water of hydration simply, it ought, in presence of so large an excess of metallic base, to be very readily expelled by heat; whereas it is actually inexpulsable by any heat whatever, short of that effecting an entire decomposition of the salt. Again, he pointed out that when the strongest nitric acid $\text{HO} \cdot \text{NO}_3$, is added, in no matter what excess, to oxide of copper, the basic salt is alone produced, apparently by a direct addition of the oxide of copper to the nitrate of water.

In 1841, Mr. Graham gave to the Chemical Society "An Account of Experiments on the Heat disengaged in Combination."† These experiments included numerous determinations of the heat evolved in the hydration of salts, and more particularly of the sulphates, including sulphate of water, or hydrated sulphuric acid. Starting from oil of vitriol $\text{HO} \cdot \text{SO}_3$, he found that each successive addition of a proportion of water HO , evolved an additional, but successively

* 'Phil. Trans.,' 1837, p. 47.

† 'Chem. Soc. Mem.,' 1, p. 106.

smaller and smaller increment of heat; and that, even after the addition of fifty proportions of water to the acid, the further addition of water was yet followed by a perceptible development of heat.

The relation of ether to alcohol being regarded as that of an oxide to its hydrate, and expressed by the formulæ C_2H_5O , and $C_2H_5O.HO$, the conversion of alcohol into ether became a matter of dehydration; and, accordingly, could not escape the examination of Mr. Graham, who, in 1850, presented to the Chemical Society some "Observations on Etherification." * The process of manufacture consisting in the distillation of a mixture of alcohol with sulphuric acid, and being attended by an intermediate production of sulphate of ether or sulphethylic acid, the substitution of ether for the basic water of sulphuric acid at one temperature, and the reverse substitution of water for the basic ether of sulphethylic acid at a higher temperature, had been represented as depending on the augmented elasticity of the ether vapour at the higher temperature. Mr. Graham showed, however, that ether could be very readily formed by heating the mixture of sulphuric acid and alcohol in sealed tubes—that is, under conditions in which the augmentation of volatility due to heat was *pari passu* counterbalanced by the diminution of volatility due to pressure. Altogether, Mr. Graham supported the contact theory of ether formation, as opposed to the then received reaction theory, but several of his experiments afforded clear, though indeed supererogatory, support to the reaction theory soon afterwards introduced by Williamson.

In addition to the memoirs cited above, the question of hydration formed an express or incidental subject of many other of Mr. Graham's investigations. It is noteworthy that, for him, osmosis became a mechanical effect of the hydration of the septum; that the interest attaching to liquid-transpiration was the alteration in rate of passage consequent on an altered hydration of the liquid; that the dialytic difference between crystalloids and colloids depended on the dehydration of the dialytic membrane by the former class of bodies only; and similarly in many other instances.

III.

Movements of Liquids under Pressure. Transpiration.—That the velocities with which different liquids, under the same pressure, issue from a hole in the side or bottom of a vessel should be inversely as the square roots of their respective specific gravities is a proposition deducible from well-known mechanical principles. As demonstrated, however, by Dr. Poiseuille, this law is not applicable to the case of liquids issuing under pressure through capillary tubes. In addition to determining experimentally the laws of the passage of the same liquid—that the velocity is directly as the pressure, inversely as the length of the capillary, and directly as the fourth power of the diameter; and that it is accelerated by elevation of temperature—

* 'Chem Soc Journ,' iii., p. 24.

Dr. Poiseuille further showed that the rate of passage of different liquids through capillary tubes is for the most part a special property of the particular liquids; and that while the rate of passage of water, for instance, is scarcely affected by the presence of certain salts in solution, it is materially accelerated by the presence of chlorides and nitrates of potassium and ammonium, and materially retarded by the presence of alkalis. He also showed that while the rate of passage of absolute alcohol is much below that of water, the rate of passage of alcohol diluted with water in such proportion as to form the hydrate, $\text{H}_6\text{C}_2\text{O} \cdot 3\text{Aq}$, is not only much below that of alcohol, but also below that of any other mixture of alcohol and water.

Some time after Dr. Poiseuille's death, Mr. Graham, starting from this last observation, took up the inquiry. Giving to the phenomenon itself the name of "transpiration," which he had previously applied to the similar passage of gases through capillary tubes, he communicated his results to the Royal Society in a paper "On Liquid Transpiration in relation to Chemical Composition."* The method he followed in his experiments was precisely that of Dr. Poiseuille, and the principal results at which he arrived are the following:—

1. That dilution with water does not effect a *pari passu* alteration in the transpiration velocity of certain liquids; but that dilution up to a certain point, corresponding to the formation of a definite hydrate, not unfrequently retards the transpiration velocity (or increases the transpiration time) to a maximum, from which the retardation gradually diminishes with further dilution. This is well seen in the following Table, giving the transpiration times of certain liquids in their undiluted state, and also the maximum transpiration times observed with the same liquids when diluted with a regularly increasing quantity of water, the particular dilution causing the maximum retardation corresponding in every case to the production of a definite hydrate.

		Transpiration Times.		
Water	H_2O ..	1·000	1·000	∞ Aq.
Sulphuric acid ..	H_2SO_4 ..	21·651	23·771	H_2SO_4 . Aq.
Nitric acid	HNO_3 ..	·990	2·103	2 HNO_3 .3 Aq.
Acetic acid	$\text{H}_4\text{C}_2\text{O}_2$..	1·280	2·704	$\text{H}_4\text{C}_2\text{O}_2$.2 Aq.
Alcohol	$\text{H}_6\text{C}_2\text{O}$..	1·195	2·787	$\text{H}_6\text{C}_2\text{O} \cdot 3$ Aq.
Wood-spirit	$\text{H}_4\text{C O}$..	·630	1·802	$\text{H}_4\text{C O} \cdot 3$ Aq.
Acetone	$\text{H}_6\text{C}_3\text{O}$..	·401	1·604	$\text{H}_6\text{C}_3\text{O} \cdot 6$ Aq.

2. That the transpiration times of homologous liquids increase regularly with the complexity of the several molecules constituting terms of the same series—certain first terms of the different series,

* 'Phil. Trans.,' 1861, p. 373

however, presenting some anomalies, as was indeed to be expected. The transpiration times of the fatty ethers are given below in illustration. Similar results were obtained with the series of fatty acids and their corresponding alcohols.

					Transpiration Times.
Water H_2O ..					1.000
Ethers	{	Formic	$H_2C_2O_2$..		.511
		Acetic	$H_3C_2O_2$..		.553
		Butyric	$H_3C_4O_2$..		.750
		Valeric	$H_3C_5O_2$..		.827

In this paper, Mr. Graham also recorded the results of two very full series of determinations of the transpiration rates of water at different temperatures between 0° and 70° ; and of two similar series of experiments made with alcohol. The transpiration velocity of water was found to increase uniformly from 0.559 at 0° to 1.000 at 20° , and thence to 2.350 at 70° ; and correlatively the transpiration times were found to decrease in the same proportion. The results obtained with alcohol were precisely similar.

IV.

Diffusion of Liquids.—Mr. Graham's early study of the spontaneous movements of gases, so as to mix with one another, naturally led him to investigate the similarly occurring movements of liquids. His results formed the subject of two papers communicated to the Royal Society, one in 1849 "On the Diffusion of Liquids,"* and the other in 1861 "On Liquid Diffusion applied to Analysis."† In the series of experiments, described in the first of these papers and in two supplementary communications, an open wide-mouthed vial, filled with a solution of some salt or other substance, was placed in a jar of water; when, in course of time, a portion of the dissolved salt, described as the diffusate, passed gradually from the vial into the external water. By experimenting in this manner, the amounts of diffusate yielded by different substances were found to vary greatly. Thus, under precisely the same conditions, common salt yielded twice as large a diffusate as Epsom salt, and this latter twice as large a diffusate as gum-arabic. Every substance examined was in this way found to have its own rate of diffusibility in the same liquid medium—the rate varying with the nature of the medium—whether water or alcohol, for instance. It is noticeable that the method of vial-diffusion resorted to in these experiments, is exactly similar to that employed by Mr. Graham in

* 'Phil. Trans.,' 1850, pp. 1, 805; 1851, p. 483.

† Ibid., 1861, p. 183.

his earliest experiments on the diffusion of gases, published in the 'Quarterly Journal of Science' for 1829.

In the series of experiments recorded in the paper "On Liquid Diffusion applied to Analysis," the solution of the salt to be diffused, instead of being placed in a vial, was conveyed by means of a pipette to the bottom of a jar of water; when, in course of time, the dissolved salt gradually rose from the bottom, through the superincumbent water, to a height or extent proportional to its diffusibility. The results of this method of jar-diffusion were found to bear out generally those attained by the method of vial-diffusion; while they further showed the absolute rate or velocity of the diffusive movement. Thus, during a fourteen days' aqueous diffusion from ten per cent. solutions of gum-arabic, Epsom salt, and common salt respectively, the gum-arabic rose only through $\frac{7}{11}$ ths of the superincumbent water, or to a height of 55.5 millimètres; the Epsom salt rose through the whole $\frac{11}{11}$ ths of superincumbent water, or to a height of 111 millimètres; and the common salt not only rose to the top, but would have risen much higher, seeing that the uppermost or fourteenth stratum of water, into which it had diffused, contained about fifteen times as much salt as was contained in the uppermost or fourteenth stratum of water into which the Epsom salt had diffused.

But of all the results obtained, the most interesting, from their bearing on various natural phenomena, were those on the partial separation of different compounds from one another, brought about by their unequal diffusibility. Thus, with a solution of equal weights of common salt and gum-arabic placed in the diffusion-vial, for every 100 milligrammes of salt not more than 22.5 milligrammes of gum were found to pass into the external water, or a separation of the salt from the gum, to this large extent, took place spontaneously by the excess of its own proper diffusive movement. Again, when a solution, containing five per cent. of common salt and five per cent. of Glauber's salt, was submitted for seven days to the process of jar-diffusion, the upper half, or $\frac{7}{11}$ ths, of superincumbent water was found to contain 380 milligrammes of common salt and only 53 grammes of Glauber's salt; or the ratio of common salt to Glauber's salt in the upper half of the liquid was as 100 to 14, the ratio in the original stratum of solution being as 100 to 100. And not only a partial separation of mixed salts, but even a partial decomposition of chemical compounds was found to result from the process of liquid diffusion. Thus the double sulphate of potassium and hydrogen, when submitted to diffusion, underwent partial decomposition into the more diffusible sulphate of hydrogen and the less diffusible sulphate of potassium; and, similarly, ordinary alum, a double sulphate of aluminum and potassium, underwent partial decomposition into the more diffusible sulphate of potassium, and the less diffusible sulphate of aluminum. Strictly speaking, perhaps, the decomposition of the original salts was not caused by, but only made evident by, the difference in diffusibility of the products.

As a general result of his experiments, Mr. Graham inferred that liquid diffusibility is not associated in any definite way with chemical composition or molecular weight. Thus he found the complex organic bodies picric acid and sugar to have much the same diffusive rates as common salt and Epsom salt respectively. Isomorphous compounds, however, proved for the most part to be equi-diffusive; although the groups of equi-diffusive substances habitually comprehended other than those which were isomorphous.

Observing further that, in many cases, the diffusion-rates of different equi-diffusive groups stood to one another in some simple numerical relation, Mr. Graham remarked that, "In liquid diffusion we no longer deal with chemical equivalents or the Daltonian atoms; but with masses even more simply related to each other by weight." We may suppose that the chemical atoms "group together in such numbers as to form new and larger molecules of equal weights for different substances, or of weights which appear to have a simple relation to each other;" and he inferred that the relative weights of these new molecules would be inversely as the square roots of the observed diffusion rates of the substances—that is inversely as the squares of their diffusion times. Thus the squares of the times of equal diffusion of hydrate, nitrate, and sulphate of potassium being 3, 6, and 12, the densities of their diffusion molecules would be as the reciprocals of these numbers, or as 1, 2, and 1.

Lastly, in comparing highly diffusive substances on the one hand, with feebly diffusive substances on the other, one broad dissimilarity became apparent, namely, that highly diffusible substances affected the crystalline state, while feebly diffusive substances were amorphous, and characterized, in particular, by a capability of forming gelatinous hydrates. Hence the distinction established by Mr. Graham between highly diffusive bodies, or *crystalloids*, and feebly diffusive bodies, or *colloids*. Compounds capable of existing both in the crystalline and gelatinous states he found to be possessed of two distinct diffusive rates corresponding respectively each to each.

V.

Dialysis and Osmose.—The subject of dialysis was included in the paper "On Liquid Diffusion applied to Analysis," referred to in the preceding section; and some further results were communicated, in 1861, to the Chemical Society, in a paper "On the Properties of Silicic Acid, and other analogous Colloidal Substances." *

In the course of his experiments on diffusion, Mr. Graham made the curious discovery that highly diffusible crystalloid bodies were able to diffuse readily, not only into free water, but also into water that was already in a low form of combination, as in the substance of a soft solid, such as jelly or membrane. Common salt, for instance, was

* Chem. Soc. Journ., xvii., p. 318

found to diffuse into a semi-solid mass of jelly, almost as easily and as extensively as into a similar bulk of free water; but the introduction of a gelatinous substance, though not interfering in any appreciable degree with the diffusion of a crystalloid, was found to arrest almost entirely the diffusion of a colloid. The colloid, of but little tendency to diffuse into free water, proved quite incapable of diffusing into water that was already in a state of combination, however feeble. Hence, although the partial separation of a highly diffusible from a feebly diffusible substance might be effected by the process of free diffusion into water, a much better result was obtained by allowing the diffusion to take place into, or through, the combined water of a soft solid such as a piece of membrane or parchment-paper. In the process of dialysis, then, crystalloid and colloid bodies, existing in solution together, are separated from one another by pouring the mixed solution into a shallow tray of membrane or parchment-paper, and letting the tray rest on the surface of a considerable excess of water, once or twice renewed. By this means the crystalloid, in process of time, diffuses completely away through the membranous septum into the free water; but the colloid, being quite incapable of permeating the membrane, however thin, is retained completely on the tray, unable to reach the free water on the other side.

By means of the process of dialysis, Mr. Graham succeeded in obtaining various colloid organic substances, such as tannin, albumen, gum, caramel, &c., in a very pure state; some of them, indeed, in a state of purity exceeding any in which they had before been met with. But the most curious results were obtained with different mineral substances, usually thrown down from their dissolved salts in the state of gelatinous or colloid precipitates. Most of these precipitates being soluble in some or other crystalloid liquid, on submitting the so-produced solutions to dialysis, the crystalloid constituents diffuse away, leaving the colloid substances in pure aqueous solution. By proceeding in this manner, Mr. Graham was able to obtain certain hydrated forms of silica, ferric oxide, alumina, chrome, prussian blue, stannic acid, titanous acid, tungstic acid, molybdic acid, &c., &c., in the state of aqueous solution,—these bodies having never before been obtained in solution, save in presence of strongly acid or alkaline compounds serving to dissolve them. Altogether, the production of these colloid solutions of substances, such as silica and alumina—in their crystalline state, as quartz and corundum, completely insoluble—threw an entirely new light upon the conditions of aqueous solution.

The colloidal solutions, obtained as above, of substances usually crystalline, were found to be exceedingly unstable. Either spontaneously, or on the addition of some or other crystalloid reagent, even in very minute quantity, they peptized or became converted into solid jellies. Hence Mr. Graham was led to speak of two colloidal states; the peptous, or dissolved, and the pectous, or gelatinized. In addition to their power of gelatinizing, their mutability, their non-crystalline habit, and their low diffusibility, substances in the colloid state were

found to be further characterized by their chemical inertness and by their high combining weights. Thus the saturating power of colloid silica was only about $\frac{1}{36}$ th of that of the ordinary acid.

In his supplementary paper communicated to the Chemical Society, Mr. Graham showed how the peptous forms of different mineral colloids could, in many cases, be reconverted into their peptous forms. He further showed how the water of different peptous and pectous colloids could be mechanically displaced by other liquids, as alcohol, glycerine, sulphuric acid, &c. To the different classes of compounds, so formed, he gave distinctive names. Thus, the alcoholic solution and jelly, of silicic acid for instance, he designated as the *alcosol* and *alcojel* respectively.

Closely associated with the passage of different liquids through membranes is the action, known as *osmosis*, discovered by Dutrochet. Mr. Graham's principal results on this subject are recorded in a very elaborate paper "On Osmotic Force," communicated to the Royal Society in 1854; * but a few further results, and a statement of his final views, are contained in the paper, referred to immediately above, "On Liquid Diffusion applied to Analysis." When the solution of a saline or other compound is separated from an adjacent mass of water by a membranous septum, a greater or less quantity of the water very commonly passes through the septum into the solution; and if the solution be contained in a vessel of suitable construction, having a broad membranous base and a narrow upright stem, the water, in some cases, flows into the vessel through the membrane, with a force sufficient to raise and sustain a column of 20 inches or more of liquid in the stem. The problem is to account for this flow; which, with acid fluids more particularly, takes place in the reverse direction—*i. e.* from the solution into the water.

In the course of his experiments, Mr. Graham examined the osmotic movement produced with liquids of most diverse character; employing osmometers of animal membrane, albuminated calico, and baked earthenware. His results were, moreover, observed and recorded in very great detail. As an illustration of these results, it may be mentioned that with 1 per cent. solutions in the membranous osmometer, the liquid rose in the stem 2 millimètres in the case of common salt, 20 millimètres with chloride of calcium, 88 millimètres with chloride of nickel, 121 millimètres with chloride of mercury, 289 millimètres with proto-chloride of tin, 351 millimètres with chloride of copper, and 540 millimètres with chloride of aluminum. Mr. Graham showed, further, in opposition to the views of Dutrochet, that the velocity of the osmotic flow was not proportional to the quantity of salt or other substance originally contained in the solution; and that the flow did not depend on capillarity, as Dutrochet had inferred; or yet on diffusion, as some of his own experiments

* 'Phil. Trans.,' 1854, p. 177.

might be thought to indicate. Eventually he was led to the conclusion that osmose was essentially dependent on a chemical action taking place between one or other of the separated liquids and the material of the septum. He appears to have held somewhat different views of the nature of this chemical action at different times; and not to have considered it as being in all cases of the same character.

The following extracts, expressing his latest views on the subject, are taken from the conclusion of his paper, "On Liquid Diffusion applied to Analysis."

"It now appears to me that the water movement in osmose is an affair of hydration and of de-hydration in the substance of the membrane, or other colloid septum, and that the diffusion of the saline solution placed within the osmometer has little or nothing to do with the osmotic result otherwise than as it affects the state of hydration of the septum. Placed in pure water, such colloids (as animal membrane) are hydrated to a higher degree than they are in neutral saline solutions. Hence the equilibrium of hydration is different on the two sides of the membrane of an osmometer. The outer surface of the membrane being in contact with pure water, tends to hydrate itself in a higher degree than the inner surface does, the latter surface being supposed to be in contact with a saline solution. When the full hydration of the outer surface extends through the thickness of the membrane, and reaches the inner surface, it there receives a check. The degree of hydration is lowered, and water must be given up by the inner layer of the membrane, and it forms the osmose. Far from promoting this separation of water, the diffusion of the salt throughout the substance of the membrane appears to impede osmose by equalizing the condition as to saline matter of the membrane through its whole thickness. The advantage which colloidal solutions have in inducing osmose, appears to depend in part upon the low diffusibility of such solutions, and their want of power to penetrate the colloidal septum."

VI.

Movements of Gases under Pressure. Effusion and Transpiration.--

The mechanical law of the passage of different gases under the same pressure through a mere perforation, as of the passage of different liquids, being that the velocities are inversely as the square roots of the specific gravities, Mr. Graham subjected this law to an experimental verification, and made known his results in a paper communicated to the Royal Society in 1846. The mode of experimenting was as follows:—A jar standing on the plate of an air-pump was kept vacuous by continued exhaustion, and a measured quantity of gas allowed to find its way into the jar through a minute aperture in a thin metallic plate. The admission of 60 cubic inches of dry air into the vacuous, or nearly vacuous jar, being arranged to take place in about 1000 seconds, the times of passage of the same volume of air were found not to vary from each other by more than two or three seconds in successive experiments.

Operating with different gases, the relative times of passage, or of "effusion," as it was denominated by Mr. Graham, proved to be approximately identical with the square roots of the specific gravities of the several gases; or, in other words, their velocities of effusion were shown experimentally to be inversely as the square roots of their specific gravities. The rate of effusion of a mixed gas corresponded in most cases with the calculated mean rate of its constituents; but the rates of effusion of the light gases, marsh gas and hydrogen, were very disproportionately retarded by the admixture with them, even to a small extent, of the heavier gases, oxygen and nitrogen.

Passing from the study of the effusion of gases through a perforated plate, Mr. Graham next submitted their "transpiration" through a capillary tube to a similarly conducted experimental inquiry. His results were communicated to the Royal Society in two very elaborate papers, "On the Motion of Gases," Parts I. and II.,* the first part containing also his above-described results on the effusion of gases. With a very short capillary, the relative rates of passage of different gases were found to approximate to their relative rates of effusion; but with every elongation of the capillary, a constantly-increasing deviation from these rates was observed—the increase of the deviation, however, becoming less and less considerable with each successive increment of elongation, until, when the tube had acquired a certain length in proportion to its diameter, a maximum deviation of the relative rates of passage of the different gases from their relative rates of effusion was arrived at. These ultimate rates of passage, unaffected in relation to each other by further elongation of the capillary, constitute the true transpiration velocities of the different gases, as distinguished from their velocities of effusion. Of all the gases experimented on, oxygen was found to have the longest transpiration time, or slowest transpiration velocity. In the following Table its time of transpiration

	Specific Gravity	✓ Specific Gravity	Transpiration Time
Hydrogen	·069	·263	·137
Marsh gas	·559	·747	·551
Nitrogen	·971	·985	·877
Oxygen	1·105	1·051	1·000
Carbonic gas ..	1·529	1·236	·730

is taken as unity, and the times of a few other gases compared therewith. In other columns are given the specific gravities of the same gases, referred to the specific gravity of air as unity; and the square roots of their specific gravities, which also express their relative times of effusion.

* 'Phil. Trans.,' 1846, p. 573; 1849, p. 349.

That gas transpiration has no direct relation to gas specific gravity is shown by the transpiration times of oxygen and nitrogen exceeding the transpiration times both of the much lighter hydrogen and marsh gas, and of the much heavier carbonic gas. Again, ammonia, olefiant gas, and cyanogen, with the different specific gravities $\cdot 590$, $\cdot 978$, and $1\cdot 806$ respectively, have the almost identical transpiration times $\cdot 511$, $\cdot 505$, and $\cdot 506$; or, approximatively, half the transpiration time of oxygen, $1\cdot 000$. Nevertheless the transpiration times of oxygen and nitrogen are directly as their specific gravities; and further, the specific gravities of nitrogen, carbonic oxide, and nitric oxide being $\cdot 971$, $\cdot 968$, and $1\cdot 039$, their transpiration times are $\cdot 877$, $\cdot 871$, and $\cdot 876$ respectively. But then olefiant gas, with the same specific gravity $\cdot 978$, has the much shorter transpiration time $\cdot 505$; and similarly in other cases. Altogether the discordance between transpiration and specific gravity is of greater frequency than the accordance; but still the circumstance of gases having the same, or about the same, specific gravity, having also the same, or about the same, rate of transpiration, is of too frequent occurrence to be merely accidental.

As a rule, the observed transpiration rate of a mixture of gases corresponded with the calculated mean rate of its constituents; but the transpiration rates of the light gases, hydrogen and marsh gas, were found to be disproportionately retarded to a greater extent even than their effusion rates by the admixture with them of heavier gases. Further, by employing mixtures of gas and vapour, Mr. Graham extended his inquiry so as to include a determination of the transpiration times of several vapours; the results being calculated on the assumption that the observed transpiration time of the mixture was the mean of the transpiration times of the permanent gas and of the coercible vapour experimented on. In this way the transpiration time of ether vapour, sp. gr. $2\cdot 586$, was shown to be identical with that of hydrogen gas, sp. gr. $0\cdot 069$; and the transpiration time of carbonic sulphide vapour, sp. gr. $2\cdot 645$, identical with that of sulphuretted hydrogen gas, sp. gr. $1\cdot 191$.

With respect to gas transpiration in general, the rates of transpiration of different gases were found to be independent of the nature of the material of the capillary; apparently from the capillary, of what material soever, becoming lined with a film of gas, with which alone the current of gas could come in contact; so that the friction was purely intestine, and suggestive of a sort of viscosity in the gas itself. The rate of passage was further shown to be inversely as the length of the capillary; and directly, in some high but undetermined ratio, as its diameter. Lastly, the rate of "effusion" of a given volume of any particular gas being independent of pressure and temperature, the rate of transpiration of a given volume of any particular gas was observed to vary directly with its variation of density, whether the result of alteration of pressure or of temperature; 100 cubic inches of dense air, for example, transpiring more rapidly than 100 cubic inches of tenuous air, in proportion to the excess of density.

Speaking of the importance and fundamental nature of the physical properties manifested by bodies in the gaseous state, and of the extent of his own inquiries on gas-transpiration, Mr. Graham observed,—“It was under this impression that I devoted an amount of time and attention to that class of constants (transpiration-velocities) which might otherwise appear disproportionate to their value and the importance of the subject. As the results, too, were entirely novel, and wholly unprovided for in the received view of the gaseous constitution, of which indeed they prove the incompleteness, it was the more necessary to verify each fact with the greatest care.”

VII.

Diffusion of Gases.—In 1801, Dalton, in an essay “On the Constitution of mixed Gases, and particularly of the Atmosphere,” propounded the now celebrated view that “where two elastic fluids denoted by A and B are mixed together, there is no mutual repulsion amongst their particles; that is, the particles of A do not repel those of B, as they do one another; consequently the pressure or whole weight upon any one particle arises solely from those of its own kind.” During the act of admixture, “the particles of A meeting with no repulsion from those of B . . . would instantaneously recede from each other as far as possible under the circumstances, and consequently arrange themselves just as in a void space.” At the beginning of 1803, in a supplementary paper “On the tendency of Elastic Fluids to Diffusion through each other,” he made known the remarkable action of intermixture which takes place, even in opposition to the influence of gravity, when any two gases are allowed to communicate with each other. Thus, in a particular experiment, he showed that when a vial of hydrogen is connected with a vial of carbonic gas by means of a narrow piece of tubing, so that the vial of light hydrogen may be inverted over the other vial of heavy carbonic gas, the heavy carbonic gas actually ascends through the light hydrogen, and the light hydrogen descends through the heavy carbonic gas until the uniform admixture of the two gases with each other is effected. The subject was afterwards investigated by Berthelot, who, in a series of experiments performed with great care, while opposing Dalton’s theoretical conclusions, corroborated his results; and indicated further the high diffusiveness of hydrogen. Here it was that Mr. Graham took up the inquiry. The first of his papers relating directly to the subject of gas-diffusion appeared in the ‘Quarterly Journal of Science’ for 1829, under the title, “A short Account of Experimental Researches on the Diffusion of Gases through each other, and their Separation by Mechanical Means.”* The mode of proceeding adopted in these researches was as follows: Each gas experimented on was allowed to diffuse from a horizontally placed bottle through a narrow tube,

* ‘Quart. Journ. Sci.’ ii., 1829, p. 83.

directed either upwards or downwards according as the gas was heavier or lighter than air, so that the diffusion always had to take place in opposition to the influence of gravity. The result was that equal volumes of different gases escaped in very unequal times, the rapidity of the escape having an inverse relation to the specific gravity of the gas. Thus hydrogen was found to escape four or five times more quickly than the twenty-two times heavier carbonic gas. Again, with a mixture of two gases, the lightest or most diffusible of the two was found to leave the bottle in largest proportion, so that a sort of mechanical separation of gases could be effected by means of their unequal diffusibility. Most of these last results were obtained by allowing the gaseous mixture to diffuse into a limited atmosphere of some other gas or vapour, capable of subsequent removal by absorption or condensation.

But these methods of operating, by free or adiabatic diffusion, were soon abandoned by Mr. Graham for the more practicable method of diffusion through porous septa. Once again, however, many years afterwards, in a paper "On the Molecular Mobility of Gases," to be more fully considered presently, Mr. Graham made some additional and very curious observations on the free diffusion of hydrogen and carbonic gas into surrounding air, showing the absolute velocities of the molecular movements in each of the two cases. A glass cylinder, 57 metre high, had the lowest tenth of its height filled with carbonic gas. Then, after different intervals of time, the uppermost tenth of air in the cylinder was drawn off and examined. In five minutes the carbonic gas in this upper tenth of air amounted to 0.4, and in seven minutes to 1.02 per cent.; or 1 per cent. of carbonic gas had diffused to the distance of half-a-metre in seven minutes, being at the rate of 73 millimètres per minute. Now, the conditions of this movement always prevail in the air of the atmosphere, and, using the words of Mr. Graham, "it is certainly most remarkable that in perfectly still air its molecules should spontaneously alter their position, and move to a distance of half-a-metre in any direction in the course of five or six minutes." By similar experiments made with an inverted cylinder, 1 per cent. of hydrogen was found to diffuse downwards at the rate of 350 millimètres per minute, or about five times as rapidly as the carbonic gas diffused upwards.

With regard to Mr. Graham's experiments on the diffusion of gases through porous septa, his earliest results on this subject were communicated to the Royal Society of Edinburgh, in a paper "On the Law of the Diffusion of Gases," already referred to as the first-born of what may be considered his great papers.* Prior even to Dalton's above-mentioned experiments on free diffusion, Dr. Priestley, when transmitting different gases through stoneware tubes surrounded by burning fuel, perceived that the tubes were porous; and that not only was

* 'Edin. Roy. Soc. Trans.,' xii., 1834, p. 222.

there an escape of the gas, under pressure, from within the tube outwards to the fire, but that there was also a penetration of the exterior gases of the fire into the tube, notwithstanding the superior pressure of the current of gas passing through the tube.

Mr. Graham, however, appears to have had his attention originally directed to the study of the transmission of gases through porous diaphragms by the curious observation and experiments of Doberciner, who, having occasion to collect and store some quantities of hydrogen over water, accidentally made use of a fissured jar, and was surprised to find that the water of the pneumatic trough rose in this jar to the height of an inch and a half in twelve hours, and to not far short of three inches in twenty-four hours. Having assured himself of the constancy of the phenomenon, Doberciner attributed it to capillary action, conceiving hydrogen to be alone attractable by, and, on account of the assumed minuteness of its atoms, admissible through the fissure. In repeating Doberciner's experiments, however, Mr. Graham soon observed that the escape of hydrogen outwards was always accompanied by a penetration of air inwards, the volume of air finding an entrance through the fissure amounting to about one-fourth of the volume of hydrogen making its escape; or the fissure proved permeable to the grosser air as well as to the finer hydrogen. Having arrived at this point, he replaced the fissured jar by an instrument admitting of much greater experimental precision. For the jar itself he substituted a piece of glass tube about half-an-inch in diameter and from eight to fourteen inches long, and for the fissure in the jar he substituted a plate of stucco serving to close one end of the tube. Operating with a diffusion-tube of this kind standing in a jar of water, it was found, as in Dalton's experiments, that the two gases, say external air and internal hydrogen, exhibited a powerful tendency to intermix or change places with each other; but more than this, it was found that the air did not exchange with its own volume of hydrogen, but instead with 3.8 times its volume. Using the word diffusion-volume to express the bulks of different gases exchanging thus with one another by the process of diffusion, the diffusion-volume of hydrogen would be 3.8, that of air being taken as 1. Similarly, it was ascertained that every gas has a diffusion-volume which is peculiar to itself, and is indeed inversely as the square root of its specific gravity; and since the unequal diffusion volumes of different gases are consequences of their unequal diffusion velocities, it follows that the relative velocities at which different gases diffuse into one another, by virtue of their own inherent mobility, are identical with those at which they effuse under pressure into a vacuum—a result quite in accordance with, and indeed deducible from, Dalton's aphorism. But although the relative rates of effusion and diffusion are alike, it is important, wrote Mr. Graham, in the later paper already quoted from, "to observe that the phenomena of effusion and diffusion are distinct and essentially different in their nature. The effusion movement affects masses of gas, the diffusion movement affects molecules; and a gas is

usually carried by the former kind of impulse with a velocity many thousand times as great as is demonstrated by the latter." *

Thus the result arrived at by Mr. Graham, in his original paper, was the enunciation of the now well-recognized law of the diffusion of gases; but, some thirty years afterwards, he again subjected the phenomena of gas-diffusion to an elaborate experimental investigation, —going over the old and penetrating into new ground with an activity by no means impaired, and with intellectual powers largely expanded by increase of years. His results were communicated to the Royal Society of London, in a paper "On the Molecular Mobility of Gases," † and it is impossible to read this and his original paper "On the Law of the Diffusion of Gases" together, without being struck by the great advance in philosophic grasp and breadth of view which had become developed in the long interval between the publication of the two memoirs. These later experiments on gas-diffusion were made principally with septa of compressed graphite; and it will be well to preface their consideration by Mr. Graham's own introductory remarks. He observes:—

"The pores of artificial graphite appear to be really so minute, that a gas *in mass* cannot penetrate the plate at all. It seems that molecules only can pass; and they may be supposed to pass wholly unimpeded by friction, for the smallest pores that can be imagined to exist in the graphite must be tunnels in magnitude to the ultimate atoms of a gaseous body. The sole motive agency appears to be that intestine movement of molecules which is now generally recognized as an essential property of the gaseous condition of matter.

"According to the physical hypothesis now generally received, a gas is represented as consisting of solid and perfectly elastic spherical particles or atoms, which move in all directions, and are animated with different degrees of velocity in different gases. Confined in a vessel, the moving particles are constantly impinging against its sides and occasionally against each other, and this contact takes place without any loss of motion, owing to the perfect elasticity of the particles. If the containing vessel be porous, like a diffusioneter, then gas is projected through the open channels, by the atomic motion described, and escapes. Simultaneously the external air is carried inwards in the same manner, and takes the place of the gas which leaves the vessel. To this atomic or molecular movement is due the elastic force, with the power to resist compression, possessed by gases. The molecular movement is accelerated by heat and retarded by cold, the tension of the gas being increased in the first instance and diminished in the second. Even when the same gas is present both within and without the vessel, or is in contact with both sides of our porous plate, the movement is sustained without abatement—molecules con-

* The motions of effusion under pressure, and of spontaneous diffusion, would appear to be alike traceable to the elasticity of the gas itself, exerted under the conditions to which it is exposed at the time.

† 'Phil. Trans.' 1863, p. 385.

tinuing to enter and leave the vessel in equal number, although nothing of the kind is indicated by change of volume or otherwise. If the gases in communication be different, but possess sensibly the same specific gravity and molecular velocity, as nitrogen and carbonic oxide do, an interchange of molecules also takes place without any change in volume. With gases opposed of unequal density and molecular velocity, the permeation ceases of course to be equal in both directions."

One set of novel experiments recorded in the later paper, from which the above remarks are extracted, had reference to the diffusion of single gases through porous septa, into a vacuum or partially vacuum space. The diffusion-tube was substantially the same as that formerly employed, except in the circumstance of its being closed by a plate of compressed graphite instead of by stucco, and in the further circumstance of the tube itself being in some cases so far lengthened and otherwise modified as to admit of the production within it of a barometric vacuum of comparatively large dimensions. The mode of experimenting was as follows:—The short tubes, when employed, were filled with mercury, and inverted in a mercurial trough. Then, by means of a very simple arrangement, the gas under examination was allowed to sweep over the surface of, and diffuse through, the graphite plate, so as to depress the mercury within the tube until it stood at a height of 100 millimètres only,—that is, until the external pressure exceeded the internal pressure by 100 millimètres only. Matters being in this state, the experiment consisted in observing the number of seconds required for the admission through the graphite septum, into the graduated tube, of a given volume of gas—the mercury in the tube being kept throughout at the constant height of 100 millimètres, by a gradual lifting up of the tube, effected by a mechanical arrangement originally devised and employed by Professor Bunsen. The long tubes were filled with mercury in a different manner; but the conduct of the experiments made with them differed only from that of the experiments made with the short tubes, in that the level of mercury in the long tubes was maintained throughout at or near to the barometric height, so that the external gas diffused into the tube under full atmospheric pressure. Experimenting

	Times of Equal Diffusion	Square Roots of Specific Gravities
Oxygen	1.0	1.0
Air9501	.9507
Carbonic gas ..	1.1860	1.1760
Hydrogen2505	.2502

in this way, the relative times of permeation of equal volumes of different gases were found to be almost identical with the square roots

of the specific gravities of the respective gases, as shown in the preceding Table.

These results are of great value from the simplicity and constancy of the conditions under which they were obtained, and from their close accordance with the induced law. By allowing the diffusion to take place into a complete or partial vacuum, instead of into an atmosphere of other gas, the results were not complicated with those of interdiffusion; and by employing a thin plate of highly-compressed graphite, instead of a comparatively thick plug of more porous stucco, the results were not complicated with those of transpiration, as happened in some otherwise admirable experiments of Professor Bunsen, which led that distinguished investigator to question at one time the accuracy of Mr. Graham's law.

The absence of any transpiration of gas through the graphite wafer was made evident by the want of any approximation, in the rates of passage, to the characteristic rates of transpiration; and was consequent on the impermeability of the exceedingly minute pores of the graphite to any enforced bodily transmission of gas through them. It may be as well to state this conclusion in Mr. Graham's own words:—

“The movement of gases through the graphite plate appears to be solely due to their own proper molecular motion, quite unaided by transpiration. It seems to be the simplest possible exhibition of the molecular or diffusive movement of gases. This pure result is to be ascribed to the wonderfully fine (minute) porosity of the graphite. The interstitial spaces appear to be sufficiently small to extinguish capillary transpiration entirely. The graphite plate is a pneumatic sieve which stops all gaseous matter in mass, and permits molecules only to pass.”

By similarly conducted experiments, a determination was also made of the difference of rate, if any, at which hydrogen diffuses through a graphite plate into a vacuum and into atmospheric air. Thus, in one minute of time, the following quantities of hydrogen passed through the graphite plate, in the two cases respectively:—

1·289 cubic centimètre into a vacuum.

1·243 cubic centimètre into air.

These numbers indicate a close approach to equality in the velocities of passage into a vacuum and into a space of other gas,—a yet closer equality being probably attainable by a modified form of experimenting.

The diffusion of hydrogen into air, as in the above-referred-to experiment, is of course accompanied by a diffusion of air into hydrogen, which had to be allowed for in calculating out the above result. Moreover, Mr. Graham made a special repetition of his early experiments on interdiffusion, operating with dry instead of moist gas, substituting mercury for water in the diffusion-tube, maintaining a constant pressure by Bunsen's mechanism instead of by

a pitcher of water, and using a wafer of graphite instead of a plug of stucco as the porous diaphragm. The theoretical exchange of hydrogen for air being 3.8 volumes for 1, and that of hydrogen for oxygen being 4.0 volumes for 1, the exchanging volumes actually found were 3.876 and 4.124 respectively.

Referring to the approximatively equally rapid passage of hydrogen into a vacuum and an aerial space, Mr. Graham remarks as follows on the subject of interdiffusion:—

“In fine, there can be little doubt left on the mind that the permeation through the graphite plate into a vacuum, and the diffusion into a gaseous atmosphere, through the same plate, are due to the same inherent mobility of the gaseous molecule. They are the exhibition of this movement in different circumstances. In interdiffusion we have two gases moved simultaneously through the passages in opposite directions, each gas under the influence of its own inherent force; while with gas on one side of the plate, and a vacuum on the other side, we have a single gas moving in one direction only. The latter case may be assimilated to the former if the vacuum be supposed to represent an infinitely light gas. It will not involve any error, therefore, to speak of both movements as gaseous diffusion,—the diffusion of gas into gas (double diffusion) in the one case, and the diffusion of gas into a vacuum (single diffusion) in the other. The inherent molecular mobility may also be justly spoken of as the diffusibility or diffusive force of gases.

“The diffusive mobility of the gaseous molecule is a property of matter, fundamental in its nature, and the source of many others. The rate of diffusibility of any gas has been said to be regulated by its specific gravity, the velocity of diffusion having been observed to vary inversely as the square root of the density of the gas. This is true, but not in the sense of the diffusibility being determined or *caused* by specific gravity. The physical basis is the molecular mobility. The degree of motion which the molecule possesses regulates the volume which the gas assumes, and is obviously one, if not the only, determining cause of the peculiar specific gravity which the gas enjoys. If it were possible to increase in a permanent manner the molecular motion of a gas, its specific gravity would be altered, and it would become a lighter gas. With the density is also associated the equivalent weight of a gaseous element, according to the doctrine of equal combining volumes.”

In addition to the above two sets of experiments, on the diffusion of a single gas into a vacuum and on the diffusion of one gas into another, a third set of experiments was made on the diffusion of one gas away from another; or on the partial separation of mixed gases by the process of atmolysis. The experiments on this subject were conducted in several different ways, but the most striking results were obtained with what Mr. Graham named his tube atmolyser. This instrument consists of one or more lengths of ordinary tobacco-pipe (conveying the current of mixed gas), surrounded by a glass tube

maintained in a more or less vacuous state by exhaustion with an air-pump. The most diffusible constituent of the mixed gas passing away in largest proportion through the porous material of the tobacco-pipe, the least diffusible constituent becomes concentrated in the residue of gas passing along, and finally delivered by the pipe. By this simple contrivance, the proportion of oxygen in ordinary air, transmitted by the tobacco-pipe, was increased from below 21 up to 24·5 per cent., as a result of the small superior diffusive velocity of nitrogen 1·01, over that of oxygen 0·95.

In experiments made with the far more unequally diffusive gases oxygen and hydrogen, mixed in equal volumes, the proportion of oxygen transmitted by the tobacco-pipe was increased from the original 50 per cent., to 90, and even in some cases to 95 per cent. Electrolytic gas, consisting of 33·3 per cent. oxygen and 66·6 per cent. hydrogen, was slowly transmitted through a single tobacco-pipe, in some experiments enclosed in a vacuum, in others exposed to the air. In the vacuum experiments the transmitted gas was found to consist of 90·7 per cent. oxygen and 9·3 per cent. hydrogen. In the air experiments, the transmitted gas was found to consist of 40·4 per cent. oxygen, 5·5 per cent. hydrogen, and 54·1 per cent. air. In both cases it had lost its explosive character, and acquired the property of re-inflaming a glowing splinter.

This paper of Mr. Graham's "On the Molecular Mobility of Gases" was supplemented by a communication made to the Chemical Society, in 1864, entitled "Speculative Ideas respecting the Constitution of Matter,"* from which the following extracts are taken:—

"It is conceivable that the various kinds of matter, now recognized as different elementary substances, may possess one and the same ultimate or atomic molecule existing in different conditions of movement. The essential unity of matter is an hypothesis in harmony with the equal action of gravity upon all bodies. We know the anxiety with which this point was investigated by Newton, and the care he took to ascertain that every kind of substance, 'metals, stones, woods, grain, salts, animal substances,' &c., are similarly accelerated in falling, and are therefore equally heavy.

"In the condition of gas, matter is deprived of numerous and varying properties, with which it appears invested when in the form of a liquid or solid. The gas exhibits only a few grand and simple features. These again may all be dependent upon atomic or molecular mobility. Let us imagine one kind of substance only to exist—ponderable matter; and further, that matter is divisible into ultimate atoms, uniform in size and weight. We shall then have one substance and a common atom. With the atom at rest the uniformity of matter would be perfect. But the atom possesses always more or less motion, due, it must be assumed, to a primordial impulse. This motion gives rise to volume. The more rapid the movement the greater the space

* 'Chem. Soc. Journ.,' xvii., p. 368.

occupied by the atom, somewhat as the orbit of a planet widens with the degree of projectile velocity. Matter is thus made to differ only in being lighter or denser matter. The specific motion of an atom being inalienable, light matter is no longer convertible into heavy matter. In short, matter of different density forms different substances—different inconvertible elements, as they have been considered.

“But further, these more and less mobile, or light and heavy forms of matter, have a singular relation connected with equality of volume. Equal volumes of two of them can coalesce together, unite their movement, and form a new atomic group, retaining the whole, the half, or some simple proportion of the original movement and consequent volume. This is chemical combination. It is directly an affair of volume, and only indirectly connected with weight. Combining weights are different, because the densities, atomic and molecular, are different. The volume of combination is uniform, but the fluids measured vary in density. This fixed combining measure—the *metron* of simple substances—weighs 1 for hydrogen, 16 for oxygen, and so on with the other ‘elements.’

“To the preceding statements respecting atomic and molecular mobility, it remains to be added that the hypothesis admits of another expression. As in the theory of light we have the alternative hypotheses of emission and undulation, so in molecular mobility the motion may be assumed to reside either in separate atoms and molecules, or in a fluid medium caused to undulate. A special rate of vibration or pulsation originally imparted to a portion of the fluid medium endows that portion of matter with an individual existence, and constitutes it a distinct substance or element.

“Lastly, molecular or diffusive mobility has an obvious bearing upon the communication of heat to gases by contact with liquid or solid surfaces. The impact of the gaseous molecule, upon a surface possessing a different temperature, appears to be the condition for the transference of heat, or the heat movement, from one to the other. The more rapid the molecular movement of the gas, the more frequent the contact with consequent communication of heat. Hence, probably, the great cooling power of hydrogen gas as compared with air or oxygen. The gases named have the same specific heat for equal volumes, but a hot object placed in hydrogen is really *touched* 3·8 times more frequently than it would be if placed in air, and 4 times more frequently than it would be if placed in an atmosphere of oxygen gas. Dalton had already ascribed this peculiarity of hydrogen to the high ‘mobility’ of that gas. The same molecular property of hydrogen recommends the application of that gas in the air-engine, where the object is to alternately heat and cool a confined volume of gas with rapidity.”

VIII.

Passage of Gases through Colloid Septa.—In 1830, Dr. Mitchell, of Philadelphia, discovered a power in gases to penetrate thin sheet

india-rubber; and, noticing the comparatively rapid transmission of carbonic gas through the rubber, associated this observation with the further one that a solid piece of india-rubber is capable of absorbing its own volume of carbonic gas, when left in contact with excess of the gas for a sufficient length of time. By means of a suitable arrangement, Dr. Mitchell found that various gases passed spontaneously through a caoutchouc membrane into an atmosphere of ordinary air with different degrees of velocity—that as much of ammonia gas was transmitted in 1 minute as of carbonic gas in $5\frac{1}{2}$ minutes, as of hydrogen in $37\frac{1}{2}$ minutes, and as of oxygen in 113 minutes. Soon after their publication, these results were ably commented on and extended by Dr. Draper, of New York; and, altogether, they attracted considerable attention in scientific circles. One of Mr. Graham's earliest observations—having reference to the spontaneous passage of carbonic gas into a moist bladder of air, so as ultimately to burst the bladder—had obviously a very close connection with Dr. Mitchell's results, and received from Mr. Graham in 1829 the same explanation that in 1866 he gave to his own india-rubber experiments, the account of which he communicated to the Royal Society in a paper “On the Absorption and Dialytic Separation of Gases by Colloid Septa.”* In his experiments on the penetration of different gases, through septa of india-rubber, into a vacuum, Mr. Graham employed a tube considerably exceeding in length the barometric column, open at one end and closed at the other by a thin film of caoutchouc stretched over a plate of highly porous stucco. On filling this tube with mercury, and inverting it into a cup of mercury, a Torricellian vacuum was left at the top, into which the external air, or any external gas experimented on, gradually found its way by passage through the caoutchouc film, so as to cause a depression of the mercurial column. By experiments made in this manner, it was found that different gases penetrated the rubber, and entered the vacuous space with the following relative velocities, differing widely from the velocities of diffusion and transpiration of the same gases given in the other two columns of the Table:—

	Rates of Passage through Caoutchouc.	Transpiration Velocities	Diffusion Velocities
Nitrogen	1.00	1.14	1.01
Marsh gas	2.15	1.81	1.34
Oxygen	2.55	1.00	.95
Hydrogen	5.50	2.29	3.80
Carbonic gas ..	13.58	1.37	.81

Bearing in mind the partial separation of gases from one another attainable by reason of their unequal diffusive velocities, the pos-

* ‘Phil. Trans.,’ 1866, p. 399.

sibility of effecting a similar separation of gases by reason of their unequal velocities of transmission through india-rubber was easily to be foreseen. For example, atmospheric air consisting of 20·8 volumes of oxygen and 79·2 volumes of nitrogen, and the transmission velocities of these two gases being respectively 2·55 and 1·0, it follows that the air transmitted through india-rubber into a vacuum should consist of 40 per cent. oxygen and 60 per cent. nitrogen, thus :—

$$\begin{array}{rcl} \text{Oxygen} & .. & 20\cdot8 \times 2\cdot55 = 53\cdot04 \\ \text{Nitrogen} & .. & 79\cdot2 \times 1\cdot0 = 79\cdot20 \\ & & \hline & & 132\cdot24 \end{array} \left. \vphantom{\begin{array}{rcl} \text{Oxygen} & .. & 20\cdot8 \times 2\cdot55 = 53\cdot04 \\ \text{Nitrogen} & .. & 79\cdot2 \times 1\cdot0 = 79\cdot20 \\ & & \hline & & 132\cdot24 \end{array}} \right\} \text{or } \left\{ \begin{array}{l} 40 \\ 60 \\ 100 \end{array} \right.$$

In subjecting this conclusion to the test of experiment, Mr. Graham availed himself of Dr. Sprengel's then newly-invented mercurial pump or exhauster, an instrument which also stood him in good stead in his subsequent work, and to which he freely acknowledged his obligations. By a slight alteration in the pump, as originally constructed, Mr. Graham made it serve not only for its original purpose of creating and maintaining an almost perfect vacuum, but also for delivering *per passu* any gas penetrating into the vacuum through its caoutchouc or other walls.

The caoutchouc films employed in these experiments were of various kinds; but the most readily practicable and, on the whole, successful results, were obtained with india-rubber varnished silk made up into a flat bag, exposing on each side about 0·25 mètre squared of surface. The interior of such a bag being in communication with the Sprengel pump, the constituents of the external air were gradually sucked through the walls of the bag and delivered by the turned-up fall-tube of the pump. On examining the delivered gas, it was found to contain on the average 41·6 per cent. of oxygen; and accordingly, to have the property of re-inflaming a glowing splinter. Thus, by the simple suction of atmospheric air through a caoutchouc film, the remarkable result was arrived at of nearly doubling the proportion of oxygen in the volume of air sucked through. Unfortunately for the practical application of the process, the entire volume of air sucked through proved to be very small, about 2·25 cubic centimètres per minute, per square mètre of surface, at 20° C. At 60° C., however, the passage of air through the rubber was almost exactly three times as rapid as at 20°.

Instead of allowing the gases experimented on to pass through the india-rubber into a vacuous space, they were in some cases allowed to pass into a space already occupied with a different gas, somewhat as in Dr. Mitchell's original experiments; but the conditions of the action were then more complex. The constituent gases of atmospheric air, for instance, pass through an india-rubber septum into a space containing carbonic gas at the relative velocities with which they enter a vacuous space; but throughout the experiment, not only are oxygen and nitrogen continually entering the space, but carbonic gas

is continually, and very rapidly, escaping from it. Eventually, by the rapid escape of carbonic gas, the proportion or pressure of oxygen in the internal space comes to exceed that in the external air; whereupon a reverse transmission, through the india-rubber, of the excess of oxygen into the external air, at once begins. But by stopping the operation at an early stage, and then absorbing the carbonic gas with caustic alkali, a residuo of hyperoxygenized air was left, capable, in some cases, of re-inflaming a glowing splinter, and containing as much as 37.1 volumes of oxygen to 62.9 volumes of nitrogen.

The interpretation, given by their discoverer to the above results, was in accordance with his slowly developed views on the relations of gases and liquids to each other and to soft solids. Having satisfied himself that the merest film of india-rubber is quite devoid of porosity, and that oxygen is at least twice as absorbable by india-rubber as by water at ordinary temperature (the absorbability of its own volume of carbonic gas by india-rubber, as by water, having been noticed by Dr. Mitchell), Mr. Graham came to view the entire phenomenon as having a very complex character,—as consisting in a dissolution of the gas in the soft india-rubber; in a diffusion of the liquefied gas, as a liquid, through the thickness of the india-rubber; in an evaporation of the liquefied gas from the internal surface of the india-rubber; and lastly in a diffusion of the evaporated gas into the internal space. Thus, in reference to the remarks of Drs. Mitchell and Draper, he writes—“These early speculations lose much of their fitness from not taking into account the two considerations already alluded to, which appear to be essential to the full comprehension of the phenomenon—namely, that gases undergo liquefaction when absorbed by liquids and such colloid substances as india-rubber, and that their transmission through liquid and colloid septa is then effected by the agency of liquid and not gaseous diffusion. Indeed, the complete suspension of the gaseous function during the transit through colloid membrane cannot be kept too much in view.” Mr. Graham seems thus to have recognized at least three distinct modes of gas transmission through a solid or semi-solid septum:—

1st. By a sufficient degree of pressure gases might be forced bodily, *i. e.* in masses, through the minute channels of a porous septum; or, in other words, might pass through such a septum by *transpiration*, of course in the direction only of the preponderating total pressure.

2nd. As the channels of a porous septum became more and more minute, their resistance to the bodily transmission of gas would become greater and greater, and the quantity of gas forced through them less and less, until at length the septum would be absolutely impermeable to transpiration under the particular pressure. But such a septum, of which the individual capillary channels were so small as to offer a frictional resistance to the passage of gas greater than the available pressure could overcome, might nevertheless present a considerable aggregate of interspace through which the *diffusion* proper

of gases, consequent on their innate molecular mobility, could take place freely in both directions.

3rd. A septum might be quite free from pores, of any kind or degree of minuteness, and so far be absolutely impermeable to the transmission of gas in the form of gas; but it might nevertheless permit a considerable transmission of certain gases by reason of their prior solution or *liquefaction* in the substance of the septum. And whereas the mere passage of gas, by transpiration or diffusion through a porous septum, would take place in thorough independence of the nature of the material of the septum, in this last considered action, the transmission would take place by virtue of a sort of chemical affinity between the gas and the material of the septum - the selective absorption of the gas by the septum being a necessary antecedent of its transmission; whence it might be said the gas was transmitted because it was first absorbed. Of course in certain transmissions two, or all three, modes of action might come into play simultaneously.

IX.

Occlusion of Gases by Metals.—The experiments of Deville and Troost having made known the curious fact of the permeability of ignited homogeneous platinum and ignited homogeneous iron to hydrogen gas, and given some indication also of the permeability of ignited iron to carbonic oxide gas, Mr. Graham, in 1866, corroborated the results of the French chemists in reference to platinum; but, modifying their method by letting the hydrogen pass into a space kept vacuum by the Sprengel pump, instead of into an atmosphere of other gas, assimilated the process to that which he had employed in his india-rubber experiments. The results he obtained were communicated to the Royal Society, partly in the paper already referred to "On the Absorption and Separation of Gases by Colloid Septa," and partly in four supplementary notices published in the Proceedings of the Society.* In carrying out the investigation forming the subject of these several communications, Mr. Graham had the advantage of being admirably seconded by his assistant, Mr. W. Chandler Roberts, whose able and zealous co-operation he repeatedly acknowledged in the warmest terms.

In the course of experiments made on the transmission of gases through ignited metallic septa, a particular platinum tube, being rendered vacuum, was found at all temperatures below redness to be quite impermeable to hydrogen; whereas at a red heat, it transmitted 100 cubic centimètres of hydrogen in half-an-hour—the quantities of oxygen, nitrogen, marsh gas, and carbonic gas, transmitted under the same conditions, not amounting to .01 cubic centimètre each in half-an-hour. It was ascertained further that, with an ignited vacuum tube of platinum surrounded by a current of ordinary coal gas (a variable

* 'Roy. Soc. Proc.' xv., p. 502; xvi., p. 422; xvii., p. 212, p. 500.

mixture of gases containing on the average about 45 per cent. of marsh gas, 40 per cent. of hydrogen, and 15 per cent. of other gases and vapours), a transmission of pure hydrogen alone took place through the heated metal. This property of selective transmission, manifested by platinum, was so far analogous to the property of selective transmission manifested by india-rubber, that whereas a septum of india-rubber transmitted the nitrogen of the air in a much smaller ratio than the oxygen, the septum of ignited platinum transmitted the other constituents of coal gas in an infinitely smaller ratio than the hydrogen. Hence the knowledge, of the absorption by india-rubber of the gases which it most freely transmitted, suggested to Mr. Graham an inquiry as to the possible absorption of hydrogen gas by platinum. Accordingly platinum, in different forms, was heated to redness, and then allowed to cool slowly in a continuous current of hydrogen. The metal so treated, and after its free exposure to the air, was placed in a porcelain tube, which was next made vacuous by the Sprengel pump. During the production and maintenance of the vacuum, no hydrogen was extracted from the metal at ordinary temperatures; or even during an hour's exposure to the temperature of 220°; or yet at a heat falling just short of redness. But at a dull red-heat and upwards, a quantity of hydrogen gas was given off amounting in volume, measured cold, to as much, in some cases, as 5.5 times the volume of the platinum. Thus was opened out to Mr. Graham the subject of his last, and probably greatest discovery—the occlusion of gases by metals. Very many metals were examined in their relations to different gases, but the most interesting results were those obtained with platinum as above described; and those obtained with silver, with iron, and above all, with palladium.

The characteristic property of silver, heated and cooled in different atmospheres, proved to be its capability of absorbing and retaining, in some cases, as much as seven times its volume of oxygen—its absorption of hydrogen falling short of a single volume. Some silver leaf, heated and cooled in ordinary air, and subsequently heated in a vacuum, gave off a mixture of oxygen and nitrogen gases containing 85 per cent. of oxygen, or more than four times the proportion contained in the original air. This remarkable property of solid silver to effect the permanent occlusion of oxygen gas, must be distinguished from the not less remarkable and doubtless associated property of melted silver to effect the temporary absorption of a yet larger volume of the same gas; which, on the solidification of the metal, is discharged with the well-known phenomenon of spitting.

Iron, though tolerably absorptive of hydrogen, was found to be specially characterized by its absorption of carbonic oxide. What may be called the natural gas of wrought iron, or the gas derived from the forge in which it was heated, proved to consist chiefly of carbonic oxide, and, in different experiments, was found to range from 7 to 12.5 times the volume of the metal; so that, in the course of its preparation, iron would appear to occlude upwards of seven times its

volume of carbonic oxide, and to carry this gas about with it ever after. The absorbability of carbonic oxide by iron has an obviously important bearing on the theory of steel production by cementation. This process would appear to consist in an absorption of carbonic oxide gas into the substance of the iron, and in a subsequent decomposition of the absorbed gas into carbon entering into combination with the metal, so as to effect its acieration, and carbonic gas discharged from the surface of the metal, so as to produce the well-known appearance of blistering. Nor is this the only, or even the chief point of interest that was made out with regard to iron; for the study of the behaviour of telluric manufactured iron naturally led Mr. Graham to the examination of sidereal native iron, that is to say, the iron of meteorites, and with the following result. A portion of meteoric iron, from the Lenarto fall, when heated in vacuo, gave off 2.85 times its volume of natural gas, of which the preponderating constituent, to the extent of 85.7 per cent. of the total quantity, consisted not of carbonic oxide, but of hydrogen, the carbonic oxide amounting to only 4.5 per cent., and the remaining 9.8 per cent. consisting of nitrogen. The inference that the meteorite had been, at some time or other, ignited in an atmosphere having hydrogen as its prevailing constituent, seems irresistible; and judging from the volume of gas yielded by the iron, the hydrogen atmosphere in which it was ignited must, in all probability, have been a highly condensed one; the charge of hydrogen extracted being fully five times as great as it was found possible to impart to ordinary iron artificially.

But it was with palladium that Mr. Graham obtained his most extraordinary results. This metal he found to have the property of transmitting hydrogen with extreme facility, even at temperatures very far short of redness. Coincidentally, at temperatures even below those requisite for transmission, palladium was found capable of absorbing many hundred times its volume of hydrogen. Thus a piece of palladium foil maintained at a temperature of 90–97° for three hours, and then allowed to cool down during an hour and a half, while surrounded by a continuous current of hydrogen gas, gave off, on being afterwards heated in vacuo, 643 times its volume of the gas, measured cold; and even at ordinary temperatures, it absorbed 376 times its volume of the gas, provided it had first been recently ignited in vacuo. In another experiment, palladium sponge, heated to 200° in a current of hydrogen and allowed to cool slowly therein, afterwards yielded 686 times its volume of the gas; while a piece of electrolytically deposited palladium heated only to 100° in hydrogen, afterwards yielded, upon ignition in vacuo, no less than 982 times its volume of the gas. The lowness of the temperature at which, under favourable circumstances, the absorption of hydrogen by palladium could thus be effected, soon suggested other means of bringing about the result. For example, a piece of palladium foil was placed in contact with a quantity of zinc undergoing solution in dilute sulphuric acid; and, on subsequent examination, was found to have absorbed 173 times its volume of hydrogen. Again, palla-

dium, in the forms of wire and foil, was made to act as the negative pole of a Bunsen's battery effecting the electrolysis of acidulated water; and in this manner was found to absorb from 800 to 950 times its volume of hydrogen in different experiments.

Palladium being thus chargeable with hydrogen in three different ways, namely, by being heated and cooled in an atmosphere of the gas; by being placed in contact with zinc dissolving in acid, *i. e.* with hydrogen in the act of evolution; and, lastly, by being made the negative electrode of a battery, —correlatively, the charged metal could be freed from its occluded hydrogen by exposing it to an increase of temperature in air or vacuo; by acting on it with different feebly oxidizing mixtures; and by making it the positive electrode of a battery.

The palladium, when charged to its maximum, was frequently found to give off a small proportion of its hydrogen, though with extreme slowness, at ordinary temperatures, both into the atmosphere and into a vacuum. But not until the temperature approached 100° was there any appreciable gas-evolution; which, above that point, took place with a facility increasing with the temperature, so as to be both rapid and complete at about 300° . Since, however, the transmission of hydrogen through heated palladium is a phenomenon of simultaneous absorption and evolution, it follows that the property of palladium to absorb hydrogen does not cease at 300° , or indeed at close upon the melting-point of gold,—the highest temperature at which Mr. Graham's experiments on transmission were conducted; but whereas the maximum absorption of hydrogen by palladium takes place at comparatively low temperatures, the velocity of transmission was observed to increase, in a rapid ratio, with the increase of temperature, indefinitely.

As regards the removal of hydrogen from palladium by oxygenants, the gas of the charged metal was found to manifest all the chemical activity of hydrogen in the nascent state. Thus it reduced corrosive sublimate to calomel, combined directly with free iodine, converted ferrid- into ferro-cyanides, destroyed the colour of permanganates, &c. Moreover, the spongy metal, charged with hydrogen and exposed to the air, was apt to become suddenly hot, and so completely discharged, by a spontaneous aerial oxidation of its absorbed gas into water; while the hydrogen of a piece of charged palladium wire was often capable of being set fire to, and of burning continuously along the wire.

Lastly, the reversal of the position of the palladium plate in the decomposing cell of the battery afforded a most ready means of completely extracting its hydrogen. Indeed, for some time after the reversal, while hydrogen was being freely evolved from the negative pole, no oxygen was observable on the surface of the palladium plate, now made the positive pole, through its rapid oxygenation of the absorbed hydrogen.

As regards the extent of the absorption of hydrogen by palladium, it was found, as already indicated, to vary considerably with the phy-

sical state of the metal, whether fused, hammered, spongy, or electrolytically deposited, for example. In one case, previously referred to, a specimen of electrolytically deposited palladium, heated to 100° , and then slowly cooled in a continuous current of hydrogen, was found to occlude 982.11 times its volume of the gas, measured cold. In this case, the actual weight of palladium experimented with, was 1.0020 gramme, and the weight of hydrogen absorbed .0073 gramme, being in the ratio of 99.277 per cent. of palladium and 0.723 per cent. of hydrogen. The atomic weight of hydrogen being 1, and that of palladium 106.5, it is observable that the ratio of the weights of the constituents of the charged metal, hydrogen and palladium, approximates to the ratios of their atomic weights.

In another experiment some palladium wire, drawn from a piece of the fused metal, was charged electrolytically with 935.67 times its volume of hydrogen. Some idea of these enormous absorptions of hydrogen may be formed by remembering that water at mean temperature absorbs only 782.7 times its volume of that most absorbable of the common gases, ammonia.

A point of interest with regard to the different quantities of hydrogen absorbable by palladium in its different states, is the gradual diminution in the absorptive power of any particular specimen of the metal, with each successive charge and discharge of gas, in whatever way effected— the absorptive power, however, being partially restorable by subjecting the metal to a welding heat.

The density of palladium charged with eight or nine hundred times its volume of hydrogen is perceptibly lowered. Owing, however, to a continuous formation of bubbles of hydrogen on the surface of the charged metal when immersed in water, there is a difficulty in taking its exact density by comparing its respective weights in air and water with one another. There is also a difficulty in determining the density by direct measurement of the charged palladium when in the form of wire; owing to the curious property of the wire, on being discharged, of not merely returning to its original volume, but of undergoing a considerable and permanent additional retraction. But in the case of certain alloys of platinum, silver, and gold with excess of palladium, while the absorptive power of the constituent palladium is still manifested, the excess of retraction on discharge of the wires does not occur; and the specific gravities deducible from the mere increase in length of wires of these alloys, are found to accord approximatively with those deducible from the increase in length of the pure palladium wire, not above its original length, but above the length to which it retracts on discharge of its absorbed gas. It would thus appear that, simultaneously with its absorption of hydrogen, the pure palladium wire, unstably stretched by the process of drawing, suffers two opposite actions; that is to say, it undergoes a process of shortening by assuming a more stable condition of cohesion, and a process of lengthening by the addition to it of other matter—the lengthening due to the additional matter being the excess of the length of the charged above

that of the discharged wire. In a particular experiment illustrative of this peculiarity, a new platinum wire took up a full charge of hydrogen electrolytically, namely, 956·3 volumes, and increased in length from 609·585 to 619·354 millimètres. With the expulsion of the hydrogen afterwards, the wire was permanently shortened to 600·115 millimètres. The sum of the two changes taken together amounts to 19·239 millimètres, and represents the true increase in the length of the wire due to the addition of hydrogen. It corresponds to a linear expansion of 3·205 in 100, or to a cubical expansion of 9·827 in 100. The original volume of the wire being ·126 cubic centimètre, the volume of the condensed hydrogen would accordingly be ·01238 cubic centimètre. Then as the charged wire, on being heated in vacuo, evolved 120·5 cubic centimètres of hydrogen gas, weighing ·0108 gramme, the density of the absorbed hydrogen would be

$$\frac{\cdot 01080}{\cdot 01238} = \cdot 872.$$

Calculated from the mere increase in length of the charged wire above that of the wire originally, the density of the absorbed hydrogen would be 1·708. The following Table gives the densities of condensed hydrogen in different experiments made with palladium wire, in which the excess of retraction on discharge was allowed for as above; and also the densities observed in experiments made with palladium alloys in which the contraction on discharge took place to the original lengths of the wires only.

When united with	Density of Condensed Hydrogen
Palladium	0·854 to 0·872
Palladium and platinum	0·7401 „ 0·7515
Palladium and gold	0·711 „ 0·715
Palladium and silver	0·727 „ 0·742

Whether the absorption of hydrogen by palladium, alloyed or not with another metal, was large or small, the density of the occluded hydrogen was found to be substantially the same. That the excessive retraction of the palladium wire on the discharge of its absorbed hydrogen is not a mere effect of heat was shown by the charged wire undergoing a similar retraction when discharged electrolytically instead of by ignition in vacuo; and also by the original wire not undergoing any sensible retraction as a result of annealing. That the retraction is merely in length was shown by the absence of any difference in specific gravity between the original and the discharged wire. Very curiously, the shortening of the wire, by successive chargings and dischargings of hydrogen, would seem to be interminable. Thus the following expansions of a particular wire, caused by variable charges of hydrogen, were followed, on expelling the hydrogen, by the contractions recorded in the other column.

		Elongation in Millimètres.	Retraction in Millimètres.
1st Experiment		9.77	9.70
2nd " 		5.765	6.20
3rd " 		2.36	3.14
4th " 		3.482	4.95
			23.99

The palladium wire, which originally measured 609.144 millimètres, thus suffered, by four successive chargings and dischargings of hydrogen, an ultimate contraction of 23.99 millimètres, or a reduction of its original length to the extent of nearly 4 per cent., each increment of contraction below the original length usually exceeding the previous increment of elongation above the original length of the wire. The alternate expansion and contraction of palladium by its occlusion and evolution of hydrogen is ingeniously shown by a contrivance of Mr. Roberts', in which a slip of palladium foil, varnished on one side, is made to curl and uncurl itself, as it becomes alternately the negative and positive electrode of a battery, or is alternately charged and discharged of hydrogen on its free surface.

That hydrogen is the vapour of a highly volatile metal has frequently been maintained on chemical grounds; and from a consideration of the physical properties of his hydrogenized palladium, Mr. Graham was led to regard it as a true alloy of palladium with hydrogen, or rather hydrogenium, in which the volatility of the latter metal was restrained by the fixity of the former, and of which the metallic aspect was equally due to both of its constituents. Although, indeed, the occlusion of upwards of 900 times its volume of hydrogen was found to lower the tenacity and electric conductivity of palladium appreciably, still the hydrogenized palladium remained possessed of a most characteristically metallic tenacity and conductivity. Thus, the tenacity of the original wire being taken as 100, the tenacity of the fully charged wire was found to be 81.29; and the electric conductivity of the original wire being 8.10, that of the hydrogenized wire was found to be 5.99. In further support of the conclusion arrived at by Mr. Graham, as to the metallic condition of the hydrogen occluded in palladium, he adduced his singular discovery of its being possessed of magnetic properties, more decided than those of palladium itself, a metal which Mr. Faraday had shown to be "feebly but truly magnetic." Operating with an electromagnet of very moderate strength, Mr. Graham found that while an oblong fragment of electrolytically deposited palladium was deflected from the equatorial by 10° only, the same fragment of metal, charged with 604.6 times its volume of hydrogen, was deflected through 48°. Thus did Mr. Graham supplement the idea of hydrogen as an invisible incondensable gas, by the idea of hydrogen as an opaque, lustrous, white metal, having a specific gravity between 0.7 and 0.8, a well-marked tenacity and conductivity, and a very decided magnetism.

[W. O.]

Friday, April 1, 1870.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

PROFESSOR H. E. ROSCOE, F.R.S.

OWENS COLLEGE, MANCHESTER,

*On the Artificial Production of Alizarine, the Colouring Principle
of Madder.*

THE speaker stated that he had to bring before the notice of his audience a discovery in organic chemistry which, whether we regard its scientific interest or its practical and commercial value, is of the highest importance, and marks an era in the history of the application of chemistry to the arts and manufactures even of greater importance than the memorable discovery made by Mr. Perkin in 1856 of the production of aniline-violet, or mauve.

Since the above-named year great progress has been made in the theoretical investigation of natural and artificial colouring matters as well as in their preparation on a large scale. The chemistry of colouring matters has now taken a high and important position, and chemists instead, as formerly was their wont, of getting rid of all colouring matters as something foreign to their objects of investigation, have, since Mr. Perkin's discovery, found out that the examination of colouring matters may not only lead to scientific laurels, but may sometimes yield fruit of another and not less acceptable kind.

We owe to the brains and hands of two German chemists, Messrs. Graebe and Liebermann, this remarkable discovery, which differs from all the former results which have been brought about by the application of science to the chemistry of colouring matters, inasmuch as this has reference to the artificial production of a natural vegetable colouring substance which has been used as a dye from time immemorial, and is still employed in enormous quantities for the production of the pink, purple, and black colours which are seen everywhere on printed calicoes, viz. *Alizarine*, the colouring principle of *Madder*.

It is from the liquid tarry products of the destructive distillation

of coal, a rich source of interest to chemists, that we now derive this new colouring matter.

The following Table contains the results of experiments made on the large scale, indicating the various yields of tar from different qualities of coal distilled in the gasworks of various towns :—

DESTRUCTIVE DISTILLATION OF COAL.

100 tons of Cannel and Bituminous Coal distilled to yield 10,000 cubic feet of gas of spec. grav. 0·6, yield the following products :—

	Gas	Tar	Ammonia Water	Coke	
1	22·25	8·50	9·50	59·75	Average of many experiments.
2	20·01	7·85	7·11	65·00	Manchester.
3	20·40	6·1	5·1	67·85	Dukinfield.
4	21·7	7·5	5·8	65·0	Macclesfield.
5	16·3	10·7	8·0	65·0	Salford.

From a careful series of experiments made by a large tar distiller, the following numbers are derived, showing the average composition of gas tar :—

100 tons of Tar on distillation yield :—

	Naphtha	Light Oils and Carbolic Acid	Heavy Oils, Naphthalene, Anthracene.	Pitch	Water, Gas, and Loss
1	3·0	1·5	35·0	50·0	10·5
2	3·0	0·8	25·0	60·0	12·2

It is from Benzol, C_6H_6 , discovered by Faraday in 1825, that the aniline colours are all of them prepared. The colour-producing power of the coal products are, however, yet far from being exhausted. It is by means of another and hitherto comparatively unknown hydro-carbon, *Anthracene*, $C_{14}H_{10}$, that the newest triumphs of the chemist have been won. This is a substance which in the pure state few chemists (even yet) have seen, and upon which only two or three had previously experimented, and yet by one happy discovery—and by an investigation which more than almost any other exhibits the value of the synthetic power of modern research this unknown body has been made to yield a colouring matter of the greatest possible value. The truth of this will at once be evident when we learn that the total growth of madder is estimated to reach 47,500 tons per annum, worth 45*l.* per ton, and having, therefore, a value of 2,150,000*l.* Of this nearly one-half is used in the United Kingdom, so that no less a sum than 1,000,000*l.* is now paid by us for madder grown in foreign

countries. This will now, in part at least, go to benefit our own population, as we can now transform our coal into this invaluable colouring matter.

In an experiment made on a large scale it was found that 100 tons of tar yielded 0·63 ton of anthracene, or 1 ton of anthracene can be obtained from the distillation of about 2000 tons of coal, not reckoning the quantity of anthracene contained in the pitch.

Madder is the root of several species of *Rubia*, amongst which the *Rubia tinctorum* is the most valued for its dyeing properties. This grows in Holland, Asia Minor, and in the south of France and of Russia. A species native to England is the *Rubia peregrina*. This belongs to the order *Rubiaceæ*, the native members of which, as the *Galium*s, are mostly inconspicuous wild plants. Some of the foreign species are on the contrary important plants, such as the *Cinchona*, *Ipecacuanha*, and Coffee plants, and these are distinguished for the number and variety of the peculiar principles which they yield, as quinine, cinchonine, caffeine, alizarine. Thanks to the kindness of Dr. Schunck, the speaker was able to show a young madder plant.

In spite of the many investigations which have been made of madder, chemists are still in doubt as to the nature of many of its constituents. Some attribute its colouring powers to the presence of at least two substances—alizarine and purpurine—whilst others say that only one of these produces the true madder colours.

Alizarine was discovered and obtained from madder, as a crystalline sublimate, by Robiquet and Colin, in 1831, but little importance attached to this discovery until Schunck, in 1848, showed that all the finest madder colours contain only alizarine combined with bases and fatty acids. The second colouring matter, termed *Purpurine*, was discovered by Persoz. It contributes to the full and fiery red colour in ordinary madder dyeing, but dyes a bad purple, alizarine being essential to the latter. Purpurine disappears during the purifying processes of soaping, &c., being far less stable than alizarine. It is distinguished from alizarine by its solubility in boiling alum liquor.

These two colouring principles may likewise be easily distinguished by the spectrum, alizarine producing a set of dark absorption-bands, quite different from those of purpurine, which again vary according to the nature of the solvent. Alizarine can be obtained in yellow needle-shaped crystals by simple sublimation from the dried madder; but this colouring matter is, singularly enough, not contained ready formed in the fresh madder root, but is the product of a peculiar decomposition. For a proof that fresh madder does not contain alizarine we have only to extract the moist root with alcohol, when neither the alcoholic extract nor the insoluble residue will be found to possess tinctorial power. We owe this knowledge to the researches of Schunck and Higgin, who have proved that alizarine is produced by a peculiar kind of fermentation which partly occurs in the root on standing, and partly takes place in the dyebeck, when the powdered madder is treated with water. A crystalline glucoside, termed *Rubianic Acid*

(Schunck), is contained in the root, and it is this which splits up simply into alizarine and glucose. This acid crystallizes in fine yellow needles, and gives a definite and crystalline potash salt, from which it was shown to contain 26 atoms of carbon in the molecule. Hence, as no other product but glucose is formed, it follows that alizarine must contain $C_{26} - C_{12} = C_{14}$. This decomposition of rubianic acid into alizarine was shown by boiling with an acid, and adding caustic soda when the blue solution of alkaline alizarine was seen. The formation of alizarine in extracts of madder root is effected by a ferment peculiar to the plant, and called Erythrozym. It is a ferment *sui generis*, since no other ferment produces the same effect. When mixed with a solution of rubian or rubianic acid, at the ordinary temperature, the latter is rapidly decomposed as with acids. This is what takes place in making *fleur de garance*. Dyers raise the temperature of their madder-baths gradually up to the boiling-point, because the application of a high temperature destroys the ferment. When the temperature is gradually raised, the ferment acts upon the glucoside, and produces alizarine.

That the colouring matter in fresh madder root is not alizarine can be easily shown by rubbing the soft portions of the root on to paper, when a yellow stain will be produced, which, on treatment with an alkali, shows the bright red colour of an alkaline solution of rubian instead of the blue solution of alizarate.

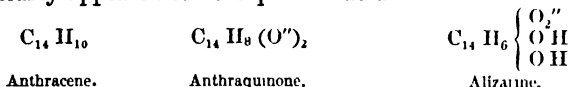
According to Schunck, the origin of purpurine, and its relation to alizarine, are still involved in obscurity.

The hypothesis which of late years has done more than any other to stimulate experiment and enlarge our views in organic chemistry is undoubtedly Kekulé's theory of the Tetrad nature of Carbon and his explanation of the constitution of the Carbon Compounds. In the so-called Paraffine group of organic substances, the carbon atoms are supposed to be connected together by single links of the four bonds attached to each atom, thus giving rise to saturated compounds by the attachment of other elements or radicals to the free bonds. In the group of aromatic substances with which we are specially concerned the carbon atoms are more closely linked together, or in other words, a less number of atoms of hydrogen are necessary to saturate an aggregation of carbon atoms than is the case in the other group. We can explain this, upon the assumption of the tetrad character of carbon, by supposing that each carbon atom is attached to its neighbour alternately by one and by two bonds.

Another singular property of these aromatic bodies is that they all contain at least six atoms of carbon and that the simplest hydrocarbon of which they are made up is Benzol C_6H_6 . So that we may regard all these aromatic compounds as Benzol derivatives, and this hydrocarbon may be considered as the skeleton round which many complicated substances are arranged. So that by the replacement of one atom of hydrogen by NH_2 we obtain Aniline, by OH Phenol, &c. From the knowledge gained by his investigation on the Quinones,

Graebe came to the conclusion that alizarine belongs to the Quinone series; and, availing themselves of Bacyer's reaction, by which Phenol can be converted into its hydrocarbon Benzol, Graebe and Liebermann passed the vapour of natural alizarine obtained from madder over heated zinc-dust, and found that the hydrocarbon they formed was identical in all its properties with Anthracene $C_{14}H_{10}$ from coal tar. Hence they confirmed Schunck's conclusions that the molecule of alizarine contains fourteen atoms of carbon. Having thus got hold of the backbone, as it were, of the compound, it only remained for them to clothe the hydrocarbon with the four additional atoms of oxygen and to take off the two atoms of hydrogen in excess, in order to obtain alizarine.

Laurent and also Anderson had, many years ago, obtained a body of the composition $C_{14}H_8O_2$, and Graebe recognized this as the Quinone of Anthracene; and he now only required to replace in this two atoms of hydrogen by two of hydroxyl (OH), in order to obtain alizarine, which clearly appeared to be a quinone acid—



This replacement of hydroxyl can be effected by Bromine, by which Bibromanthraquinone $C_{14}H_6Br_2O_2$ is formed, and this, on fusion with caustic potash, gives potassium alizarate, yielding pure alizarine on treatment with hydrochloric acid. The high price of bromine rendered this process unavailable for manufacturing purposes, and hence another plan was simultaneously proposed by several chemists for effecting the same end in a cheaper mode. Use was hereby made of Kekulé's and Wurtz's reaction in the formation of sulphobenzolic acid. On treating Anthraquinone with strong sulphuric acid to a high temperature, the di-sulpho acid $C_{14}H_6O_2 \left\{ \begin{array}{l} SO_3H \\ SO_3H \end{array} \right.$ is formed, and this, on heating with concentrated solution of potash, yields the sulphite and alizarate of potassium; from the latter substance pure alizarine is obtained by the action of acids.

In the following Table we have a statement of the synthetic production of alizarine from its constituent elements:—

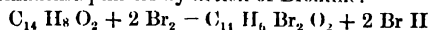
SYNTHESIS OF ALIZARINE.

1. Acetylene by direct union of Carbon and Hydrogen in Electric Arc.
 $C_2 + H_2 = C_2H_2$ (Berthelot, 1862.)
2. Benzol (Tri-acetylene) from Acetylene by Heat.
 $3 C_2H_2 = C_6H_6$ (Berthelot, 1866.)
3. Anthracene from Benzol and Ethylene.
 $2 C_6H_6 + C_2H_4 = C_{14}H_{10} + 3 H_2$ (Berthelot, 1866.)
4. Alizarine from Anthracene. (Process No. 1.)
(Graebe and Liebermann, 1869.)

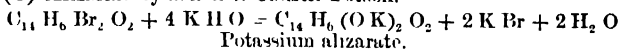
(A) Oxyanthracene or Anthraquinone by Nitric Acid.
 $C_{14}H_6(OH)_2$ (Anderson, 1861.)

SYNTHESIS OF ALIZARINE—*continued*.

(B) Bibromanthraquinone by action of Bromine.



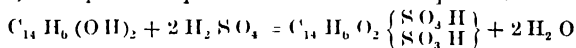
(C) Alizarine by action of Caustic Potash.



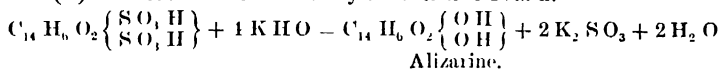
5. Alizarine from Anthracene. (Process No. 2.)

(Graebe and Caro, Perkin, Schorlemmer and Dale.)

(A) Disulphoanthraquinonic Acid from Anthraquinone.



(B) Alizarine from the above by the action of Potash.



Mr. Perkin states that an intermediate substance is formed in this reaction having the formula $\text{C}_{14} \text{H}_6 (\text{O})_2'' \left\{ \begin{array}{l} \text{O K} \\ \text{O S O}_3 \end{array} \right\}$, and this, when heated with potash, splits up into alizarine and a sulphite. Other yellow-coloured products are, according to Perkin, contained in the alizarine as sent out from his manufactory. The nature of these yellow crystalline bodies is as yet unknown.

Of the identity of the natural with the artificial alizarine there can be no doubt: they agree in all their physical and chemical properties. Their absorption-spectra are identical, their tinctorial powers are the same; the coloured lakes which they form with alumina, iron, and copper salts are of the same tint and possess the same degree of solubility, and these remain alike unaltered by the action of light, so that when they are fixed in the cotton-fibre they yield equally fast colours.

It is difficult to predict how far the artificial alizarine will in future restrict the growth of madder; but there is no doubt that for many styles of calico-printing the artificial alizarine is of the greatest value, and we may naturally expect to see very important changes effected in this branch of chemical industry in the further practical application of this new discovery.

CONTRIBUTIONS TO THE HISTORY OF ALIZARINE. $\text{C}_{14} \text{H}_8 \text{O}_4$.

1825. Faraday discovered Benzol in Coal-gas Oil. $\text{C}_6 \text{H}_6$.
 1831. Robiquet and Colin discovered Alizarine in Madder Root.
 1832. Dumas and Laurent discovered Anthracene in Coal Oils.
 1848. Schunck gave the Composition of Alizarine. $\text{C}_{14} \text{H}_{10} \text{O}_4$.
 1850. Strecker " " " " $\text{C}_{10} \text{H}_6 \text{O}_3$.
 1862. Anderson examined Anthracene Compounds. $\text{C}_{14} \text{H}_{10}$.
 1865. Kekulé explained the constitution of the Aromatic Compounds.
 1866. Baeyer obtained Benzol from Phenol.
 1868. Graebe investigated the Quinones.
 1868. Graebe and Liebermann obtained Anthracene from Alizarine.
 1869. " " " " Alizarine from Anthracene.

[H. E. R.]

Friday, June 10, 1870.

SIR H. HOLLAND, Bt. M.D. D.C.L. F.R.S. President, in the Chair.

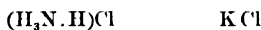
WILLIAM ODLING, M.B. F.R.S.

FLITTIERIAN PROFESSOR OF CHEMISTRY, ROYAL INSTITUTE,

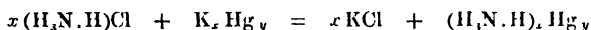
On the Ammonia Compounds of Platinum.

FOR nearly a century past ammonia gas, discovered by Priestley in 1774, has been a subject of extreme interest to chemists. This ammonia gas, H_3N , is especially characterized by its property of uniting directly with hydrochloric acid gas, HCl , to form a solid deposit of sal-ammoniac, or hydrochloride of ammonia, $\text{H}_3\text{N}.\text{HCl}$.

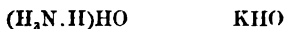
In several important particulars, sal-ammoniac presents a remarkable similarity of behaviour to chloride of potassium; and, by linking together the hydrogen of its acid with its ammonia so as to form the grouping $\text{H}_3\text{N}.\text{H}$ or H_4N , it may be regarded as the chloride of a composite metal ammonium, just as potassium chloride is the chloride of the simple metal potassium; thus:—



Ordinarily, when potassium chloride is subjected to the action of a weak current, no potassium, but only potash, makes its appearance at the negative pole; but if the negative pole be constituted of a drop of mercury, the electrolytically-liberated potassium remains dissolved in the mercury as potassium-amalgam $\text{K}.\text{Hg}_y$. Similarly, when solution of sal-ammoniac is subjected to electrolysis, the negative pole being constituted of mercury, there is produced a bulky amalgam of ammonium— $(\text{H}_3\text{N}.\text{H})_x.\text{Hg}_y$; which, however, when no longer under the influence of the current, speedily breaks up into ammonia, hydrogen, and mercury. Ammonium-amalgam may further be produced on a large scale by the action of potassium-amalgam or sodium-amalgam on sal-ammoniac solution, thus:—

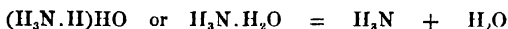


Another characteristic property of ammonia gas is its extreme solubility in water. By its dissolution it furnishes a liquid having many of the properties of aqueous potash, as, for example, the properties of affecting test-paper, of neutralizing acids, and of precipitating metallic salts. And just as sal-ammoniac may be regarded as a chloride of ammonium, analogous to chloride of potassium, so may aqueous ammonia be regarded as a hydrate of ammonium analogous to hydrate of potassium, thus:—



But whereas chloride of ammonium, analogous to chloride of potassium, constitutes a definite body,—hydrate of ammonium, analogous to hydrate of potassium, has an inferential existence only. It is

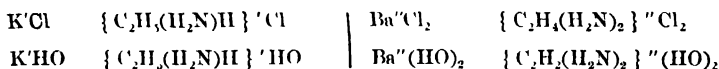
inferred to exist in solution from the reactions of the solution ; but, under all attempts at extraction, it breaks up into ammonia gas and water, thus :—



But by far the most interesting circumstance with regard to ammonia is its property, so remarkably developed by Hofmann, of serving as a type from which compounds of the most varied character are derivable by substitution. Just, for example, as the hydrocarbon residue, or radical, ethyl C_2H_5 , can replace the hydrogen of hydrochloric acid to form ethylic chloride $\text{C}_2\text{H}_5.\text{Cl}$, so can it also replace the hydrogen of ammonia to form ethylamine $\text{C}_2\text{H}_5.\text{H}_2\text{N}$. This ethylamine constitutes a very volatile liquid, vaporizing considerably even at ordinary temperatures. Its vapour closely resembles ammonia gas, but is distinguishable therefrom by its ready inflammability. Like ammonia, ethylamine combines directly with hydrochloric acid to form ethylamine sal-ammoniac, or hydrochloride of ethylamine $\text{C}_2\text{H}_5.\text{H}_2\text{N}.\text{HCl}$. Like ammonia, also, ethylamine is extremely soluble in water ; and its solution, like that of ammonia, behaves in many respects as a definite hydrate $\text{C}_2\text{H}_5.\text{H}_2\text{N}.\text{H}_2\text{O}$, not obtainable, however, in the isolated state, but, like hydrate of ammonia, known only in the state of solution.

There exist, moreover, derivatives of ammonia in which a portion of its hydrogen is replaced, not by a monad, but by a diad residue or radical. Just, for example, as diad ethylene, C_2H_4 , replaces the hydrogen of two units of hydrochloric acid to form ethylenic chloride, $\text{C}_2\text{H}_4.\text{Cl}_2$, so can it also replace, in part, the hydrogen of two units of ammonia to form ethylenamine, $\text{C}_2\text{H}_4(\text{H}_2\text{N})_2$ or $(\text{C}_2\text{H}_4)''\text{H}_2\text{N}_2$. This double ammonia unites with *two* units of hydrochloric acid to form the definite hydrochloride, $\text{C}_2\text{H}_4(\text{H}_2\text{N})_2.2\text{HCl}$, and with *two* units of water to form the equally definite, stable, isolable, volatile, crystallizable hydrate $\text{C}_2\text{H}_4(\text{H}_2\text{N})_2.2\text{H}_2\text{O}$.

The hydrochloride and non-isolable hydrate of ethylamine being compared with the chloride and hydrate of the monad alkali-metal potassium, the hydrochloride and isolable hydrate of ethylenamine are similarly comparable with the chloride and hydrate of the diad alkali-metal barium, thus :—



And hydrate of ethylenamine agrees with hydrate of barium, as well in being a powerfully alkaline base, as in being de-hydrateable, not by the action of heat, but by indirect methods only.

Through the further researches of Hofmann, chemists are acquainted with ammonias and di-ammonias, in which, not only one-third, but two-thirds and three-thirds of the hydrogen are replaced by monad ethyl and diad ethylene respectively. With regard to these compounds, both in their properties and in the nature of the

hydrochlorides and hydrates which they furnish, di- and tri-ethylamine correspond very closely to ethylamine—di- and tri-ethylenamine very closely to ethylenamine.

	Ethylamines.			Ethylenamines.	
Mono-	(C ₂ H ₅)H ₂ N	..		(C ₂ H ₄) ^{''} H ₄ N ₂	
Di-	(C ₂ H ₅) ₂ HN	..		(C ₂ H ₄) ^{''} ₂ H ₂ N ₂	
Tri-	(C ₂ H ₅) ₃ N	..		(C ₂ H ₄) ^{''} ₃ N ₂	

Although, in this way, the principal developments and ultimate establishment of the idea of ammonia as a type have resulted from investigations in organic chemistry, the idea itself appears to have originated in the first instance from investigations made in mineral chemistry; and especially from the investigation of compounds formed by the reaction of certain metallic salts and ammonia. Graham, indeed, had early represented certain compounds of metallic chlorides with ammonia as being metallicized sal-ammoniacs; but the notion of ammonia as a trihydric type, susceptible of three successive degrees of substitution, was first enunciated by Laurent, and was employed by that most original chemist to explain, among other matters, the constitution of different ammoniated compounds of platinum, discovered by Magnus, Gros, and Reiset successively. These compounds he represented as being salts of derived ammonias, in which different proportions of the hydrogen of ammonia were replaced by platinum.

Platinum is a moderately hard, pewter-coloured metal, possessed of many singular properties. It was first recognized as a distinct metal by Wood, an assayer of Jamaica, in 1711. The mode of working it was discovered and practised by Wollaston early in the present century, and described by him in the 'Philosophical Transactions' for 1829. Platinum is especially characterized by its high specific gravity; by its low conductivity, dilatability, and specific heat; by its high ductility and tenacity; by its facile divisibility and reducibility; by its curious absorptivity of certain gases, more especially hydrogen; by its difficult attackability by chemical agents; and by its infusibility at the highest furnace heats. And by each of these several properties, except perhaps its high specific gravity, is it suited to some special application in the arts.

Chemically, platinum is characterized by its high atomic weight, 197; and by its formation of two well-defined chlorides, —a perchloride, also known as platinic chloride, expressed by the formula Pt^{'''}Cl₄, and a protochloride, also known as platinous chloride, expressed by the formula Pt^{''}Cl₂. Platinic chloride occurs in crystalline, dark orange masses, freely soluble in water. Platinous chloride forms an olive-brown amorphous powder, quite insoluble in water, but dissolving in hydrochloric acid to form an ochre-coloured liquid. In 1828, the late Professor Magnus, by supersaturating this liquid with ammonia, obtained a remarkable compound, containing the elements of platinous chloride and ammonia, and presenting itself as a dull green, usually crystalline, precipitate. This notable green precipitate has formed the subject of

frequent investigation from then till now; and different views of its constitution, from time to time, have been put forward. But no one of these views has received a sufficiently general acceptance to warrant the designation of the compound in accordance therewith; so that, from the period of its discovery down to the present day, it has ever borne the honoured name of its discoverer, and been known as the green salt of Magnus.

Some time after, Gros, in 1838, by treating the salt of Magnus with nitric acid, obtained a peculiar series of pale yellow, or colourless, platin-ammonia compounds. Next, in 1840-44 *et seq.*, Reiset and Peyrone, by acting on the salt of Magnus, or on platinous chloride itself, with ammonia, obtained, independently of each other, two additional series of compounds, having relations of metamorphosis both with one another and with the foregoing series of Gros. Then, in 1846, Raewsky, by acting on the salt of Magnus with nitric acid, obtained yet another series of compounds, differing from those furnished to Gros by the same reagent.

But the formulæ, attributed by Raewsky to the salts which he had just discovered, were inconsistent both with Laurent's view of ammonia as a type, and with other views of chemical constitution which those illustrious fellow-workers Laurent and Gerhardt shared in common. Accordingly, Gerhardt, in 1848, subjected Raewsky's formulæ,—notwithstanding their corroboration by a Committee of the Academy,—to a most trenchant criticism; and after supplementing his criticism by laboratory research, published in 1850, his celebrated memoir "On the Ammoniacal Compounds of Platinum." In this memoir he established the existence of another, entirely new, series of platin-ammonia compounds; he showed, by experiment, the simple relationship in which the salts of Raewsky stand to the salts of Gros; and he set forth a complete, self-consistent scheme of viewing the several series of platin-ammonia compounds in their relations to ammonia and to one another.

Since the publication of Gerhardt's memoir, further important contributions to the knowledge of platin-ammonia compounds have been made by different chemists, especially by Buckton, Hadow, and Thomsen. But neither before nor since has any complete general scheme of the constitution of this class of bodies been put forward. Nevertheless the scheme of Gerhardt, though always treated with respect, has never met with general acceptance, and nowadays, at any rate, is open to very serious objections.*

The attention of the writer having of late been directed to the study of these compounds, he has succeeded in differentiating the simplest of the platinum sal-ammoniacs from several allied and isomeric bodies with which it had before been confounded; and in obtain-

* Gerhardt's own base platinumine, for instance, is represented by the certainly improbable formula Pt, HN or $\text{Pt}''\text{HN}$, and its hydrochloride by the yet more improbable formula $\text{Pt}, \text{HN}, 2\text{HCl}$; in which the unit of a mon-ammonia is represented as combined with two units of hydrochloric acid, and by which the entire chlorine of the salt is represented as fulfilling one and the same function.

ing from it the corresponding hydrated base of the series. He has also obtained some reactions of interest with bodies belonging to the more complex series; and, as a general result of his inquiries, has ventured to put forward a new scheme of regarding the entire group of bodies. This scheme is based on the recognition of two principal facts or propositions:—

1°. The different platin-ammonia compounds are produced in the first instance from platinous chloride PtCl_2 ; and just as the platinum of this compound possesses the property of taking up two additional proportions of chlorine so as to furnish the platinic compound Cl_2PtCl_2 or $\text{Pt}^{\text{III}}\text{Cl}_4$, so also does the platinum of the different ammoniated bodies obtained from platinous chloride possess the property of taking up two proportions of chlorine, or its equivalent of other negative radical, so as to furnish platinic compounds corresponding to the original platinous compounds respectively. Hence the division of platin-ammonia compounds into the two classes of platinous and platinic; the compounds of the former, differing in constitution from those of the latter class, just as platinic differs from platinous chloride, by a direct fixation of chlorine.

2°. The monad residue or radical amidogen H_2N , is capable of becoming the monad radical ammon-amidogen $\text{H}_2\text{N}.\text{H}_2\text{N}$ or H_4N_2 , just as the monad radical methyl H_2C , is capable of becoming the monad radical methylen-methyl or ethyl $\text{H}_2\text{C}.\text{H}_2\text{C}$ or H_4C_2 .* Viewing sal-ammoniac $\text{H}_2\text{N}.\text{HCl}$ as the analogue of methylic chloride $\text{H}_2\text{C}.\text{HCl}$, the difference is noticeable, that while the ammonia both of sal-ammoniac and ammon-amidogen is easily separable, the methylen both of methylic chloride and methylen-methyl is inseparable from the remaining constituents of the respective compounds. Hence the distinction between the two classes of amic and ammon-amic platinum compounds, the latter differing from the former by an actual addition of diad ammonia, much as ethylic differ from methylic compounds by a virtual addition of diad methylen. The parallelism is indicated in the under-written formulæ for methylic chloride and ethylic chloride, sal-ammoniac and ammonio-chloride of silver, respectively:—



The group of platin-ammonia compounds is thus divisible into the two classes of platinous and platinic; and each of these again into the two classes of amic and ammon-amic compounds. To these four classes must yet be added a fifth sub-class of di-platinic compounds, including the nitrate-chloride of Racowsky and the subsequently-discovered nitrate of Gerhardt and chloride of Hadow. The scheme of the constitution of the entire group, in accordance with the writer's views, is exhibited in the accompanying table of the principal chloride, hydrate, nitrate and nitrite compounds.

* 'Phil. Mag.' 1869, p. 459.

PLATINUM BASES AND SALTS.

PROPOSED SCHEME.

<i>Platosamine.</i>	<i>Amo-platosamine (Reiset's).</i>
$\text{Pt}''(\text{H}_2\text{N})_2 \cdot 2\text{HCl}$	$\text{Pt}''(\text{H}_3\text{N}_2)_2 \cdot 2\text{HCl} \cdot \text{Aq.}$
$\text{Pt}''(\text{H}_2\text{N})_2 \cdot 2\text{H}(\text{HO})$	$\text{Pt}''(\text{H}_3\text{N}_2)_2 \cdot 2\text{H}(\text{HO})$
$\text{Pt}''(\text{H}_2\text{N})_2 \cdot 2\text{H}(\text{NO}_3)$	$\text{Pt}''(\text{H}_3\text{N}_2)_2 \cdot 2\text{H}(\text{NO}_3)$
<i>Platinamine (Gerhardt's).</i>	<i>Amo-platinamine (Gros').</i>
$\text{Cl}_2\text{Pt}'''(\text{H}_2\text{N})_2 \cdot 2\text{HCl}$	$\text{Cl}_2\text{Pt}'''(\text{H}_3\text{N}_2)_2 \cdot 2\text{HCl}$
$\text{Cl}_2\text{Pt}'''(\text{H}_2\text{N})_2 \cdot 2\text{H}(\text{HO}) ?$	$\text{Cl}_2\text{Pt}'''(\text{H}_3\text{N}_2)_2 \cdot 2\text{H}(\text{NO}_3)$
$(\text{HO})_2\text{Pt}'''(\text{H}_2\text{N})_2 \cdot 2\text{H}(\text{HO})$	$(\text{HO})_2\text{Pt}'''(\text{H}_3\text{N}_2)_2 \cdot 2\text{H}(\text{NO}_3)$
$\text{OPt}'''(\text{H}_2\text{N})_2 \cdot 2\text{H}(\text{NO}_3) \cdot 3\text{Aq} ?$	$(\text{NO}_2)_2\text{Pt}'''(\text{H}_3\text{N}_2)_2 \cdot 2\text{H}(\text{NO}_3)$
$(\text{NO}_3)_2\text{Pt}'''(\text{H}_2\text{N})_2 \cdot 2\text{H}(\text{NO}_3)$	$(\text{NO}_2)_2\text{Pt}'''(\text{H}_3\text{N}_2)_2 \cdot 2\text{HCl}$
<i>Amo-di-platinami</i> (Raewsky's, &c)	$\left\{ \begin{array}{l} \text{Cl}_2\text{OPt}_2'''(\text{H}_3\text{N}_2)_4 \cdot 4\text{HCl} \\ \text{Cl}_2\text{OPt}_2'''(\text{H}_3\text{N}_2)_4 \cdot 4\text{HNO}_3 \cdot \text{Aq} \\ (\text{NO}_3)_2\text{OPt}_2'''(\text{H}_3\text{N}_2)_4 \cdot 4\text{HNO}_3 \cdot \text{Aq.} \end{array} \right.$

Platosamine.

The hydrochloride is obtainable by direct action of platinous chloride $\text{Pt}''\text{Cl}_2$ on ammonia, just as ethylenamine hydrochloride is obtainable by direct action of ethylenic chloride $(\text{C}_2\text{H}_4)''\text{Cl}_2$ on ammonia; and, in both reactions, the two compounds are each accompanied by various other products. The parallelism, in constitution and properties, of the two compounds and of their corresponding hydrates is complete:—



Hydrochloride of platosamine, in its pure state, has a dull, very pale, primrose colour, approaching almost to white. It is very insoluble in cold, considerably more soluble in hot water.* From its concentrated hot solution it is usually deposited as a flocculent-looking, though really crystalline, or partly crystalline, precipitate; and by slow cooling of the solution, it may be obtained wholly in the form of distinct needles. The base is obtained from the hydrochloride, through the intervention of the sulphate, by decomposing the latter with baryta water. It is extremely soluble in water, and readily crystallizable. It furnishes a solution manifesting a strongly alkaline reaction, liberating ammonia from its salts, neutralizing acids, absorbing carbonic acid from the air, and decomposing metallic salts—the precipitates thrown down being, however, for the most part double compounds.

* The orange-yellow, scaly, far more soluble hydrochloride, obtained by dissolving salt of Magnus in sulphate of ammonia solution, is a distinct compound.

The base and other soluble platosamine compounds are characterized by giving with hydrochloric acid a precipitate of the hydrochloride, which, when formed in this way, is almost always yellow and crystalline. All platosamine compounds, including the hydrochloride, exhibit the platinous property of absorbing chlorine, and hence of decolourizing a mixture of hydrochloric acid and permanganate, to yield platinamine compounds; and they all, including the hydrochloride, dissolve in gently-heated ammonia, to yield their corresponding amo-platosamine compounds.

Amo-platosamine.

The hydrochloride of this series, unlike that of the preceding, is freely soluble in water. It is a beautiful salt, crystallizing usually in a mass of interlaced lengthy needles. It is made by dissolving platinous chloride, salt of Magnus, or the above platosamine hydrochloride, in aqueous ammonia at a gentle heat. The hydrated base is obtained from it, as is the preceding hydrated base from the preceding hydrochloride. The so-produced hydrate corresponds in its general properties with the above hydrate of platosamine, than which, however, it is far more powerfully alkaline. From different metallic salts it throws down the respective metallic hydrates.

Amo-platosamine salts, like those of platosamine, exhibit the platinous property of decolourizing a mixture of hydrochloric acid and permanganate, of directly absorbing chlorine or bromine, and also of directly absorbing nitric peroxide, to furnish amo-platinic compounds.* The resulting amo-platinic chloro-chloride occurs as a pale yellow, the nitro-chloride as a pale green, and the nitro-nitrate as a pale blue precipitate. Amo-platosamine is further distinguished from platosamine by the free solubility of its hydrochloride, and by the reaction of this salt with platinous chloride solution to throw down the green salt of Magnus.

Platinic Compounds.

The most characteristic of the salts of platinamine is the chloride $(Cl_2Pt'''(H_2N)_2 \cdot 2HCl)$. It is best made by addition of permanganate, in very slight excess, to a hot solution of platosamine hydrochloride, acidified with hydrochloric acid. It is a beautiful bright yellow salt, dissolving sparingly in cold, moderately, though, on account of its density, somewhat slowly, in boiling water; and crystallizing readily on cooling in isolated octahedrons or square plates. It reacts with excess of ammonia, at a gentle heat, to form the insoluble chloride of amo-platinamine. Its chlorine, like that of the amo-platinic chloride, is evidently in two different conditions of attackability by reagents, such as alkalis and silver salts. The hydrate of platinamine is ob-

* The reaction of amo-platosamine compounds with nitric peroxide was discovered by Hadow, but received from him a different interpretation.

tained from the hydrate-nitrate, by means of ammonia, as a neutral, almost insoluble, bright yellow, crystalline precipitate.

The best known salt of amino-platinamine is the chloro-nitrate $\text{Cl}_2\text{Pt}'''(\text{N}_2\text{H})_2 \cdot 2\text{HNO}_3$, obtained by treating the salt of Magnus, or preferably the hydrochloride of amino-platosamine, with nitric acid. It is moderately soluble in water, and crystallizes therefrom in brilliant white flat prisms. Its chlorine is not immediately recognizable by nitrate of silver; and is only partially precipitable thereby, even after long boiling. Its solution yields, with ammonium chloride and sodium sulphate, crystalline white precipitates of the chloro-chloride and chloro-sulphate respectively.

The most familiar salt of amino-di-platinamine is the chloroxy-nitrate $\text{Cl}_2\text{OPt}_2'''(\text{H}_2\text{N})_4 \cdot 4\text{HNO}_3 \cdot \text{Aq.}$ It is best made by boiling the chloro-nitrate or chloro-chloride of amino-platinamine with nitric acid and nitrate of silver. It presents considerable resemblance to the chloro-nitrate of amino-platinamine, but its solution is not disturbed either by sulphate of sodium or chloride of ammonium. It yields moreover, with platinous chloride solution, a moss-like coppery precipitate which is highly characteristic (Hadow).

[W. O.]

Friday, January 20, 1871.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

JOHN TYNDALL, Esq. LL.D. F.R.S.

PROFESSOR OF NATURAL PHILOSOPHY IN THE ROYAL INSTITUTION,

*On the Colour of Water, and on the Scattering of Light in Water
and in Air.*

The Method of Research.

By the term "scattering" employed in the title of this discourse I intend to denote the irregular reflexion of light from particles mechanically suspended in water or in air. Such particles, you know, reveal themselves along the track of a beam of light when it passes through a dark room. Such a beam, wide at some parts and powerfully concentrated at others, is now before you, the space it occupies being accurately revealed by the floating notes. We can abolish this scattering either by the withdrawal of the light or by the destruction of the floating matter. I partially intercept this beam; the space corresponding to the intercepted portion is dark, because there no light is scattered. I destroy the matter by burning it, and spaces of darkness immediately appear where a moment ago we had myriads of shining notes. These experiments are familiar to most of you. To see these effects aright, it is necessary that the eye should receive light from the floating dust alone, which is thus differentiated, as philosophers say, from the unilluminated space around it. This point is easily illustrated by means of the sun-burners which illuminate this room. When the gas is turned on the track of the beam sinks in brilliancy; when the gas is turned off the strength of the beam is augmented.

The Oran Eclipse Expedition.

During the last two or three years I have been looking much at illuminated dust, and from what I have heard or read of that halo or glory called the corona, which is seen around the sun during total eclipses, I thought it might be caused by a kind of solar dust, cast possibly into space by the enormous agitations and explosions to which

the sun's photosphere is known to be subject. Thoughts of this kind—and they were not the only ones—made me wish to see the corona, and I therefore availed myself of the permission courteously granted me to accompany the Eclipse Expedition to Oran. Every member of the expedition was, I believe, perfectly prepared through previous discipline to do his duty efficiently, and if the party was defeated it certainly was not through any misdeeds of its own.

From the roof of the bastionet on which I had placed the excellent instrument lent to me by my friend, Mr. Warren de la Rue, I witnessed a very striking effect, which connects itself with this subject of the scattering of light. When all hope had vanished, and the darkness was obviously falling towards totality, I abandoned the telescope and looked towards a distant ridge, where I knew the darkness would first appear. At this time a vast fan of beams, issuing from the hidden sun, covered all the southern sky. These beams, as you know, are alternations of light and shadow, produced by cloudlets of various degrees of density, floating in illuminated haze. The beams are really parallel, but by the effect of perspective they appear divergent, like a fan. The darkness took possession of the ridge to which I have referred, and immediately afterwards passed over the region of the beams, blotting them out as if a sponge had been passed over them. It then took possession of three successive patches of blue sky in the south-eastern heaven. I again looked towards the ridge where the darkness first appeared. A glimmer like a dawn was behind it, and immediately afterwards the fan of beams, which had been for two minutes obscured, revived in all its strength and splendour. The eclipse was ended, we had been defeated, and nothing remained but to strangle disappointment by taking up other work.

The Colours of Sea Water.

The colour of the sea had long interested me, and on my way out I collected a number of bottles of water, with a view to subsequent examination. But my bottles were claret bottles, and I could by no means feel sure of their purity. At Gibraltar, therefore, I purchased fifteen white glass bottles, with ground-glass stoppers, and at Cadiz, on my return, I secured a dozen more. These seven-and-twenty bottles were filled with water, taken at different places along the line between Algeria and Spithead.

And here it is most fit that I should express my acknowledgments to Captain Henderson, the commander of H.M.S. 'Urgent,' who aided me in my observations in every possible way. Indeed, my thanks are due to all the officers for their unfailing courtesy and help. The captain placed at my disposal his own coxswain, a handsome intelligent fellow named Thorogood, who skilfully attached a cord to each bottle, weighted it with lead, cast it into the sea, and after three successive rinsings, filled it under my own eyes. The contact of jugs, buckets, and other vessels, was thus avoided, and even the necessity of pouring the water out afterwards through the dirty London air.

The process of examination to which these bottles were subjected after my return to London is in some sense complementary to that of the microscope, and may, I think, materially aid inquiries conducted with that instrument. In microscopic examination attention is directed to a small portion of the liquid, and the aim is to detect the individual suspended particles. By the method I pursued, a large portion of the liquid is illuminated, its general condition being revealed, through the light scattered by suspended particles. Care is taken to defend the eye from the access of all other light, and thus defended, it becomes an organ of inconceivable delicacy. Were the water perfectly free from matter, in a state of mechanical suspension, it would, in my opinion, scatter no light at all. The track of a luminous beam could not, I think, be seen in such water. But an amount of impurity so infinitesimal as to be scarcely expressible in numbers, and the individual particles of which are so small as wholly to elude the microscope, may, when examined by the method alluded to, produce not only sensible but striking effects upon the eye.

For the sake of sparing time, let us direct our attention to these nineteen bottles, filled at various places between Gibraltar and Spithead. The results of the examination of the water in these nineteen bottles are tabulated before you. We have first three specimens of water, described as green, a clearer green, and bright green, taken in Gibraltar Harbour, at a point two miles from the harbour, and off Cabreta Point. What does the home examination reveal about these waters? It says that the first was thick with suspended matter, the second less thick, and the third still less thick. The green brightened as the suspended matter became less. We now pass suddenly into indigo water. What change does the home examination here reveal? The water becomes suddenly augmented in purity, for the suspended matter has become suddenly less. Off Tarifa, the deep indigo disappears, and the sea is undecided in colour. Accompanying this change, we have a rise in the quantity of suspended matter. Beyond Tarifa, we change to cobalt-blue, the suspended matter falling at the same time in quantity. This water is distinctly purer than the green. We approach Cadiz, and at twelve miles from the city get into yellow-green water; this the London examination shows to be thick with suspended matter. The same is true of Cadiz Harbour, and also of a point fourteen miles from Cadiz in the homeward direction. Here there is a sudden change from yellow-green to a bright emerald green, and accompanying the change a sudden fall in the quantity of suspended matter. Between Cape St. Mary and Cape St. Vincent the water changes to the deepest indigo. In point of purity, this indigo water is shown by home examination to transcend the emerald-green water.

We now reach the remarkable group of rocks called the Burlings, and find the water between the shore and the rocks a strong green; the home examination shows it to be thick with fine matter. Fifteen or twenty miles beyond the Burlings we come again into indigo water, from which the suspended matter has in great part disappeared. Off

Cape Finisterre, about the place where the 'Captain' went down, the water becomes green, and the home examination pronounces it to be thicker. Then we enter the Bay of Biscay, where the indigo resumes its powers, and where the home examination shows the greatly augmented purity of the water. A second specimen of water taken from the Bay of Biscay held in suspension fine particles of a peculiar kind; the size of them was such as to render the water richly iridescent. It showed itself green, blue, or salmon colour, according to the direction of the line of vision. Looked at obliquely *from* the light the water was blue. Finally, we come to our last two bottles, the one taken opposite St. Catherine's Lighthouse, in the Isle of Wight, the other at Spithead. The sea at both these places was green, and both specimens, as might be expected, were pronounced by the home examination to be thick with suspended matter.

Two distinct series of observations have been thus brought before you, the one consisting of direct observations of the colour of the sea, conducted during the voyage from Gibraltar to Portsmouth; the other conducted in our laboratory below stairs. And here it is to be noted that in the home examination I never knew what water I had in my hands. The labels, which had written upon them the names of the localities, had been tied up as you see them here, all information regarding the source of the water being thus precluded. The bottles were simply numbered, and not till all the waters had been examined did I open the labels, and ascertain the locality and sea colours corresponding to the various specimens. I must, therefore, have been perfectly unbiassed in my home observations, and they establish beyond a doubt the association of the green colour of sea water with fine suspended matter, and the association of the ultramarine colour, and more especially of the black indigo hue of sea water, with the comparative absence of such suspended matter.

The Causes of the Colours of the Sea.

Let us clear our way by a few experiments towards an explanation of the dark hue of the deep ocean.* Colour, you know, resides in white light, appearing generally when any constituent of the white light is withdrawn. Here is a liquid which colours a beam sent through it purple, and this colour is immediately accounted for by the action of the solution on a spectrum. It cuts out the yellow and green, and allows red and blue to pass through. The blending of these two colours produces the purple. Does the liquid allow absolutely free passage to the red and blue? No. It enfeebles the whole

* A note written to me the 22nd of October, by my friend Canon Kingsley, contains the following reference to this point:—"I have never seen the Lake of Geneva, but I thought of the brilliant, dazzling dark blue of the mid Atlantic under the sunlight, and its black blue under cloud, both so solid that one might leap off the sponson on to it without fear; this was to me the most wonderful thing which I saw on my voyage to and from the West Indies."—J. T.

spectrum, but attacks with special energy the yellow and green colours. By increasing the thickness of the stratum traversed by the beam, we cut off the whole of the spectrum. Through the deeper layer, which I now place in the path of the beam, no colour can pass. Here, again, is a blue liquid. Why is it blue? Its action on the spectrum answers the question. It first extinguishes the red; then as the thickness augments it attacks the orange, yellow, and green in succession; the blue alone finally remains, but everything might be extinguished by a sufficient depth of the liquid.

And now we are prepared for a concentrated but tolerably complete statement of the action of sea water upon light, to which it owes its blackness. Here is our spectrum. This embraces three classes of rays—the thermal, the visual, and the chemical. These divisions overlap each other; the thermal rays are in part visual, the visual rays in part chemical, and *vice versa*. The vast body of thermal rays is here beyond the red and invisible. They are attacked with exceeding energy by water. They are absorbed close to the surface of the sea, and are the great agents in evaporation. At the same time the whole spectrum suffers enfeeblement; water attacks all its rays, but with different degrees of energy. Of the visual rays the red are attacked first, and first extinguished. While the red is extinguished, the remaining colours are enfeebled. As the solar beam plunges deeper into the sea, orange follows red, yellow follows orange, green follows yellow, and the various shades of blue, where the water is deep enough, follow green. Absolute extinction of the solar beam would be the consequence if the water were deep and uniform, and contained no suspended matter. Such water would be as black as ink. A reflected glimmer of ordinary light would reach us from its surface, as it would from the surface of actual ink; but no light, hence no colour, would reach us from the body of the water. In very clear and very deep sea water this condition is approximately fulfilled, and hence the extraordinary darkness of such water. The indigo, to which I have already referred, is, I believe, to be ascribed in part to the suspended matter, which is never absent, even in the purest natural water, and in part to the slight reflexion of the light from the limiting surfaces of strata of different densities. A modicum of light is thus thrown back to the eye, before the depth necessary to absolute extinction has been attained. An effect precisely similar occurs under the moraines of the Swiss glaciers. The ice here is exceptionally compact, and owing to the absence of the internal scattering common in bubbled ice, the light plunges into the mass, is extinguished, and the perfectly clear ice presents an appearance of pitchy blackness.

The green colour of the sea when it contains matter in a state of mechanical suspension has now to be accounted for; and here, again, let us fall back upon the sure basis of experiment. This white plate was once a complete dinner-plate, very thick and strong. It is, you see, surrounded securely by cord, and to it a lead weight is fastened. Forty or fifty yards of strong hempen line were attached to the plate.

With it in his hand, my assistant, Thorogood, occupied a boat fastened as usual to the davits of the 'Urgent,' while I occupied a second boat nearer to the stern of the ship. He cast the plate as a mariner heaves the lead, and by the time it had reached me, it had sunk a considerable depth in the water. In all cases the hue of this plate was green, not, of course, a pure green, but a mixture of green and blue; and when the sea was of the darkest indigo, the green was the most vivid and pronounced. I could notice the gradual deepening of the colour as the plate sank, but at its greatest depth in indigo water the colour was still a blue green.

Other observations confirmed this one. The 'Urgent' is a screw steamer, and right over the blades of the screw there was an orifice called the screw-well, through which you could look from the poop down upon the screw. The surface glimmer which so pesters the eye was here in a great measure removed. Midway down a plank crossed the screw well from side to side, and on this I used to place myself to observe the action of the screw underneath. The eye was rendered sensitive by the moderation of the light; and still further to remove all disturbing causes, Lieutenant Walton had the great kindness to have a sail and tarpaulin thrown over the mouth of the well. Underneath this I perched myself, and watched the screw. In an indigo sea the play of colours was indescribably beautiful, and the contrast between the water which had the screw-blades for a background, and that which had the bottom of the ocean as a background, was extraordinary. The one was of the most brilliant green, the other of the most lustrous ultramarine. The surface of the water above the screw-blade was always ruffled. Liquid lenses were thus formed, by which the coloured light was withdrawn from some places and concentrated upon others. The screw-blades in this case replaced the plate in the former case, and there were other instances of a similar kind. The hue from an indigo sea was always green at a certain depth below the surface. The white bellies of the porpoises showed the same hue, varying in intensity as the creatures swung to and fro between the surface and the deeper water. In a rough sea the light which had penetrated the summit of a wave sometimes reached the eye. A beautiful green cap was thus placed upon the wave when the ship was in indigo water.

But how is this colour to be connected with the suspended particles? Take the dinner-plate which showed so brilliant a green when thrown into indigo water. Suppose it to diminish in size until it reached an almost microscopic magnitude. It would still behave substantially as the larger plate, sending to the eye its modicum of green light. If the plate, instead of being a large coherent mass, were ground to a powder sufficiently fine, and in this condition diffused through the clear sea water, it would send green to the eye. In fact, the suspended particles which the home examination revealed in green sea water act in all essential particulars like the plate, or like the screw-blades, or like the foam, or like the bellies of the porpoises.

When too gross, or in too great quantity, the suspended particles thicken the sea itself visibly. But when sufficiently small, but not too small, and when sufficiently diffused, they do not sensibly interfere with the limpid greenness of the sea itself. They then require the stronger and more delicate test of the concentrated luminous beam to reveal their presence.

Suspended Particles in Drinking-water.

The method employed here, and which is one of extreme simplicity, may be extended. It may of course be applied to the examination of ordinary water, and when this is done unexpected results are sometimes obtained. Here, for instance, is a bottle of water intended to quench the lecturer's thirst, and it would be well for the lecturer not to scrutinize it too closely. In the track of the beam of light it simply reveals itself as dirty water. So you see that we are invaded with dirt not only in the air we breathe, but in the water we drink. And this water is no worse than the other London waters. Thanks to the kindness of Professor Frankland, I have been furnished with specimens of the water of eight London companies. They are all laden with impurities mechanically suspended. But you will ask whether filtering will not remove the suspended matter? The grosser matter, undoubtedly, but not the more finely-divided matter. Here is water which has been passed four times through a filter of bibulous paper, but it is still laden with fine matter. Here, also, is a bottle kindly lent me by Mr. Lipscomb, and passed once through his charcoal filter. But the track of the beam through it is more luminous than through air, because the quantity of matter suspended in the water is greater than what is suspended in air. Here is another specimen courteously sent to me by the Silicated Carbon Company. All the grosser matter has been removed, but it is thick with fine matter. Nine-tenths of the light scattered by these particles is perfectly polarized in a direction at right angles to the beam, and this release of the particles from the ordinary law of polarization is a demonstration of their smallness. I should say by far the greater number of the particles concerned in this scattering are wholly beyond the range of the microscope. They are so small that I do not think that any filter can intercept them. I do not want to frighten you in any way, for our drinking-water may be harmless—it may be only nasty. There is an æsthetic pleasure in the drinking of a glass of cold sparkling water, and I fear these experiments will destroy this pleasure if you ever enjoyed it. And it is next to impossible by artificial means to produce a pure water. Mr. Hartley, for example, some time ago distilled water while it was surrounded by hydrogen, but the water was not free from floating matter. Here is a specimen obtained from the combustion of water in air, the aqueous vapour being condensed by the polished surface of a chilled silver basin. When shaken up it is full of fluff and particles, coarse and fine. It is so hard to be clean in the midst of dirt. Here, however, is an approach to pure water. It is from the Lake of Geneva,

and the bottle was carefully filled for me by my distinguished friend Sorot. The water has remained quiet for a good while, and its purity is in part to be ascribed to the subsidence of the particles. The track of the beam through it is of a delicate sky-blue; there is scarcely a trace of grosser matter.

The purest water that I have obtained — probably the purest which has been seen hitherto — has been obtained from the fusion of selected specimens of ice. But extraordinary precautions are required to obtain this degree of purity. Here is an apparatus devised and constructed by Mr. Cottrell for this purpose. Through the plate of an air pump passes the shank of a large funnel, attached to which below the plate is a series of glass bulbs. In the funnel is placed a block of the most transparent ice, and over the funnel is a glass receiver. This is first exhausted and refilled several times with air, which has been filtered by its passage through cotton wool, the ice being thus surrounded by absolutely pure moteless air. But the ice has previously been in contact with mote-filled air; it is therefore necessary to let it wash its own face, and wash the bulb which is to receive the water of liquefaction. The ice is permitted to melt, the bulb is filled several times and emptied several times, until finally the large block dwindles to a small one. We may be sure that all impurity has been thus removed from the surface of the ice. These two bulbs contain water obtained in this way, the purity of which is the maximum hitherto attained. Still I should hesitate to call the water absolutely pure. When the concentrated beam is sent through it the track of the beam is not invisible, but of the most exquisitely delicate blue. This blue is purer than that of the sky, so the matter which produces it must be finer than that of the sky. Looked at perpendicularly to the beam the blue may be quite quenched by a Nicol's prism. It may be, and indeed has been, contended that this blue is scattered by the very molecules of the water, and not by matter suspended in it. But when we remember that this perfection of blue is approached gradually through stages of less perfect blue, and when we remember that a blue in all respects similar is demonstrably obtainable from particles mechanically suspended, we should hesitate, I think, to conclude that we have arrived here at the last stage of purification. The evidence, I think, points distinctly to the conclusion that could we push the process of purification still farther, even this last delicate trace of blue would disappear.

Dr. Bence Jones proposed to me a few days ago to express numerically the degrees of impurity arising from mechanical suspension. This ice water might be called the standard, or "1," all higher degrees of impurity being marked by higher numbers. Such a method would undoubtedly give distinctness to our language in speaking of water. But my aim is to point out a means of extreme simplicity by which microscopic examination may be powerfully aided and supplemented. Five minutes' inspection of a water in this way will teach you more regarding the quantity of impurity than whole days spent with the

microscope. The microscope is rightly employed in determining the character of the individual particles which are revealed *en masse* by the luminous beam.

Drinking-water from Chalk Districts.

But is it not possible to match the water of the Lake of Geneva here in England? Undoubtedly it is. We have in England a kind of rock which constitutes at once an exceedingly clean recipient and a natural filter of extraordinary efficacy, and from which we can obtain water extremely free from mechanical impurities. I refer to the chalk formation, in which large quantities of water are held in store. Our chalk hills are in most cases covered with thin layers of soil, and with very scanty vegetation. Neither opposes much obstacle to the entry of the rain into the chalk, where any organic impurity which the water may carry in is soon oxidized and rendered harmless. Those who have scampered like myself over the downs of Hants and Wilts will remember the scarcity of water in those regions. In fact, the rainfall, instead of washing the surface and collecting in streams, sinks into the fissured chalk and percolates through it, and when this formation is suitably tapped we obtain water of exceeding briskness and purity. Here is a large globe filled with the water of a well near Tring. It is wonderfully free from mechanical impurity; indeed, it stands to reason that water wholly withdrawn from surface contamination and percolating through so clean a substance should be pure. Sending a beam through this glass of water its purity is conspicuous; you see the track of the beam, but it is not the thick and muddy track revealed in London waters. It has been a subject much debated whether the supply of excellent water which the chalk holds in store could not be rendered available for London. Many of the most eminent engineers and chemists have ardently recommended this source, and have sought to show that not only is its purity unrivalled but that its quantity is practically inexhaustible. Data sufficient to test this are now, I believe, in existence; the number of wells sunk in the chalk is so considerable and the quantity of water which they yield is so well known.

But this water, so admirable as regards freedom from mechanical impurity, labours under the disadvantage of being very hard. It is rendered hard by the large quantity of carbonate of lime which it holds in solution. The chalk water in the neighbourhood of Watford holds in solution about 17 grains of carbonate of lime per gallon. This, in the old terminology, used to be called 17 degrees of hardness. Now this hard water is bad for tea, bad for washing. It furs your boilers, because the lime held in solution is precipitated by boiling. If the water be used cold its hardness must be neutralized at the expense of soap before it will give a lather. I remember being struck by the enormous quantity of soap wasted in a washing establishment in Hampshire through the hardness of the water. This of itself would seem an insuperable objection to the use of chalk water in

London. But the objection has now been successfully met by the experimental demonstration that such water can be softened inexpensively and on a grand scale. I had long known the method of softening water called Clark's process, but not until recently did I see proof of its application in the case of large communities. The chalk water is softened by Mr. Homersham at Caterham, at Canterbury, and at the Chiltern Hills for the supply of Tring, Aylesbury, and other places.

I have visited all these places, and made myself acquainted with the works. At Canterbury there are three reservoirs covered in and protected by a concrete roof and layers of pebbles both from the summer's heat and the winter's cold. Each reservoir contains 120,000 gallons of chalk water. Adjacent to these reservoirs are others containing pure slaked lime—the so-called “cream of lime.” These are filled with water, the lime and water being thoroughly mixed by air forced in by an engine through apertures in the bottom of the reservoir. The water thus well mixed with the lime soon dissolves all of this substance that it is capable of dissolving. The lime is then allowed to subside to the bottom, leaving a perfectly clear lime water behind.

The object is now to soften the chalk water. Let us suppose one of the three large reservoirs empty; into this is introduced a certain quantity of the clear lime water, and after this about nine times the quantity of the chalk water. The transparency immediately disappears—the mixture of the two clear liquids becomes thickly turbid. The carbonate of lime is precipitated, and the reservoir being now full the precipitate is permitted to subside; it is crystalline and heavy, and therefore sinks rapidly. In about twelve hours you find a layer of pure white carbonate of lime at the bottom of the reservoir, with a water of extraordinary beauty and purity overhead. A few days ago I pitched some halfpence into a reservoir 16 feet deep at the Chiltern Hills. The 16 feet hardly perceptibly dimmed the coin. Had I cast a pin in, it could, I am persuaded, have been seen at the bottom. By this process of softening the water is reduced from about 17 degrees of hardness to 3 degrees of hardness. It yields a lather immediately. Its temperature is constant throughout the year. In the hottest summer it is cool; it does not freeze in winter if conveyed in proper pipes. It is not exposed to the contamination of either earth or air. The reservoirs are covered; a leaf cannot blow into it, no surface contamination can reach it, it passes direct from the main into the house-tap; no cisterns are employed, the supply is always fresh and pure. It is highly charged with air. This is the kind of water which is supplied to the fortunate people of Canterbury.

Let me show you a specimen of this softened water, and as the eye is eminently an organ of relation, needing comparison to judge aright, I will subject to the gauge-test a globe of water taken out of our cistern down-stairs, and a globe of water taken a few days ago from one of the reservoirs at the Chiltern Hills. Here are two electric

lamps, connected with two batteries down-stairs. I send the beams through both of them, first permitting the globes themselves to act as lenses, and afterwards converging the beams upon them with glass lenses. You can judge of the difference without any word of mine.

The Water Supply of London.

The purity and goodness of this chalk water are demonstrable, and if we like it hard we can have it hard; if we like it soft we can have it soft. It lends itself to our purposes with perfect flexibility; the sole doubtful question is the adequacy of the supply for three millions of people. But let us take some common ground. On all hands it will be admitted that large—I will not say “vast” quantities of this beautiful water run to waste. Why should this be permitted? If the chalk is unable to supply the wants of three millions, it is certainly able to supply the wants of a smaller number. Supposing it competent to promote health, cleanliness, and comfort among one-third of the population of London, why not apply it to these uses? Why should a valuable treasure be lost, because it does not possess three times its actual value?

Let your expectations be as moderate as you like, only make the trial. That trial, of which the success is demonstrable, will solve the larger question whether the chalk is able to supply the whole of London. In moral matters it is our duty to realize our best insight. Let us do so here. By honestly doing what we can with this chalk water, we shall learn the limits of our action. A small good is certainly within our reach, and by accepting it we may disclose possibly an incalculable benefit to London.

[J. T.]

Friday, January 27, 1871.

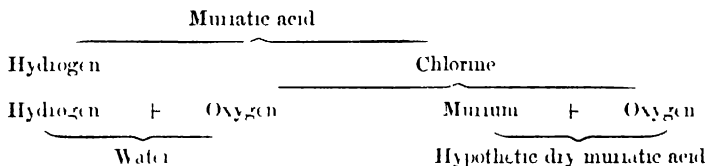
SIR HENRY HOLLAND, Bart. M.D. D C.L. F.R.S. President, in the Chair.

WILLIAM ODLING, M.B. F.R.S.

FULFRIAN PROFESSOR OF CHEMISTRY, ROYAL INSTITUTION,

On Improvements in the Manufacture of Chlorine.

CHLORINE gas was first obtained in 1774 by the Swedish chemist, Scheele, as a product of the action of muriatic acid—or marine acid, as it was then called—on the black earthy mineral manganese. In accordance with the theoretical notions of the day, Scheele gave to his newly-discovered aerial substance the name dephlogisticated marine acid, which, translated into the language of the new Lavoisierian school, became afterwards oxy-muriatic acid. Its assumed constitution, and relationship to muriatic acid are indicated below.

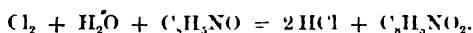


But Davy, in 1810, showed that muriatic acid gas is a substance wholly free from water, and a definite compound of Scheele's gas with hydrogen. He showed further that Scheele's gas, the so called oxy-muriatic acid, was not only incapable of furnishing oxygen under any circumstance whatever; but that, so far as experience went, it was altogether undecomposable. Being thus an undecomposed and apparently undecomposable substance, he proposed to regard it as an element, and to designate it, from its yellowish-green colour, by the name chlorine, which it has ever since borne. After considerable opposition, especially on the part of Berzelius, who subsequently, however, became a convert, the view of Davy at length prevailed, and has ever since held its ground, not indeed without occasional challenging, from time to time. Thus Schonbein, in several of his letters to Faraday, maintained very strongly the superior truthfulness of the original view; and still more recently Brodie has represented the comparable units of hydrogen H , muriatic acid HCl , and chlorine Cl , by the symbols α , $\alpha\chi$, and $\alpha\chi^2$, implying that the units of muriatic acid and chlorine differ from the unit of hydrogen by a combination of the matter of α with the matter of χ and with the matter of χ^2 , re-

spectively. But whatever may hereafter prove to be its real nature, chlorine has hitherto proved undecomposable, and is accordingly regarded by the generality of chemists as an element.

Coincident with the discovery of chlorine itself was the discovery of its most characteristic property, that of bleaching vegetable colours. The petals and leaves of plants, infusions of their several colouring matters, as well as fabrics dyed with the several colouring matters, were found to be rapidly bleached when treated either with chlorine gas, or with a solution of the gas in water. From the rapid action of the gas and its solution on pronounced vegetable colours, Berthollet in 1785 conceived the notion that chlorine in one form or other might be used with advantage commercially for the bleaching of calicoes and linens, theretofore always bleached by a tedious exposure to air and sunlight. The processes devised by Berthollet for carrying out the new method of bleaching were introduced into Scotland in 1787, and soon afterwards became extensively employed. Woven fabrics were bleached by immersion in chlorine water, and paper-pulp more especially by exposure to chlorine gas.

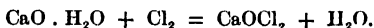
The bleaching action of chlorine takes place only in presence of water or moisture, and is dependent on the property of chlorine under suitable circumstances to decompose water, by uniting with its hydrogen to form muriatic acid, and so setting free its oxygen, by which the bleaching is really effected. Thus when chlorine, blue indigo, and water are present together, the opposite tendencies of the chlorine to take hydrogen, and of the indigo to take oxygen from the water, are satisfied by the production of chloride of hydrogen or muriatic acid on the one hand, and of oxide of indigo or isatin on the other, this isatin being a soluble orange-red non-tinctorial body :



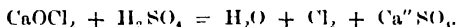
Thus bleaching by the action of chlorine, like bleaching by exposure to air, is really an act of oxidation.

But the action of chlorine on vegetable fabrics is not confined to that of bleaching their attached colouring matter; the fibre of the fabric is itself liable to be attacked both by the free chlorine and the muriatic acid to which it gives origin. Hence it became important to find a substitute for the free chlorine which should have, like it, the property of liberating nascent oxygen so as to bleach, but should not have, at any rate in the same degree, the property of corrosiveness so as to destroy. Such a substitute is offered in the familiar compound known as bleaching powder, introduced into commerce by the Messrs. Tennant, of Glasgow, in the year 1799. This substance is made by exposing slaked lime to an atmosphere of chlorine gas. The chlorine enters into combination with the lime of the slaked lime, to furnish a product which in practice contains some 35 per cent. of its weight of chlorine, and consists of a definite compound of lime with its own

weight of chlorine, plus a variable excess of slaked lime unacted upon :



Bleaching powder occurs as a dry white pulverulent solid, having a characteristic smell, allied to but not identical with that of weak chlorine. It dissolves considerably in water to form a yellow-tinted liquid, known as bleaching liquor, having a marked alkaline reaction from the presence in it of excess of lime. Coloured goods immersed for a longer or shorter time in bleaching liquor of greater or less strength and temperature, gradually have their colouring constituents destroyed or oxidated, the bleaching salt CaOCl_2 , losing its oxygen, and becoming changed into chloride of calcium, CaCl_2 . It is observable that the bleaching or liberation of nascent oxygen from bleaching powder is much slower than the bleaching or liberation of nascent oxygen by means of free chlorine; to such an extent, indeed, that for many purposes bleaching powder would be quite inapplicable, were it not for the property it has of liberating chlorine on acidification, whereby a still indirect but yet almost immediate oxidation is effected. Ten grains of bleaching powder, for instance, mixed with a little sulphuric or muriatic acid, will evolve some four cubic inches of chlorine gas :



The superior activity of the chlorine liberated by acidification of bleaching liquor to the original bleaching liquor, is taken advantage of commercially. Brown linens, for example, are first steeped in weak bleaching liquor with little apparent result, and then "soured" by immersion in dilute acid, whereby an immediate more or less complete bleaching is effected. Again, in what is known as the "discharge style" patterns or designs are printed with a mixture of gum and tartaric or other acid, upon a red or blue ground, and the printed fabric passed through a solution of bleach. The red or blue ground withstands the feebler action of the bleach, but the acid printed pattern becomes completely decolorized by the chlorine set free locally, as a result of the action of the acid upon the bleach. It is to this facility of management and capability of being used in different ways that the great utility of bleaching powder and its consequent enormous consumption are due. The amount of bleaching powder made annually in Great Britain and Ireland at the present time is estimated at 75,000 tons, representing at the price of ten pounds a ton, a value of three-quarters of a million sterling.

Bleaching powder being formed by exposing slaked lime to an atmosphere of chlorine, the manufacture of bleaching powder involves the production of chlorine. Indeed, chlorine is produced at chemical works almost exclusively for the manufacture of bleaching powder, and of one other product, namely, chlorate of potash. This latter is made to the extent of about 750 tons per annum, having at the price

of one hundred and five pounds per ton, a value of nearly 80,000*l.* sterling.

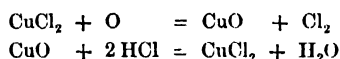
The original reaction upon one another of muriatic acid and peroxide of manganese, by which Scheele was led to the discovery of chlorine, is the basis of the manufacturing process which has ever since been almost exclusively followed. The action consists essentially in the excessive oxygen of the peroxide taking away the hydrogen of the muriatic acid and so setting its chlorine free. Peroxide of manganese, more often called simply manganese, is one of that very limited class of native mineral substances containing an excess of oxygen; the only other similarly peroxidized substance abundant in nature being nitre, in its two forms of East Indian or potash-nitre, and Chilian or soda-nitre. Now, when muriatic acid instead of being acted on by manganese is acted on by nitre, or by the nitric acid, formerly known as spirit of nitre, produced therefrom, the excessive oxygen of the nitre takes away hydrogen from the muriatic acid and sets its chlorine free. Thus by addition of nitric acid or nitre to aqueous muriatic acid a solution of chlorine is produced, recognizable in various ways, and especially by its power of dissolving gold leaf. Now, although nitre or nitric acid is a much more expensive oxygenant than manganese it was conceived that nitric acid might nevertheless be substituted with advantage for manganese, from the circumstance that after it had given up its excessive oxygen so as to liberate the chlorine of the muriatic acid, its deoxidized residue could readily acquire fresh oxygen from the atmosphere, and so reproduce nitric acid, to be used as an oxygenant over and over again indefinitely; and, indeed, the nitric method of producing chlorine has for some time past been to a limited extent in actual use.

With regard to manganese, however, until recently no means have been known of causing its deoxidized residue to re-acquire oxygen from the air, and so become in a condition to serve again for the liberation of chlorine. From time to time, more particularly by Messrs. Tennant and Mr. Wm. Gossage, attempts have been made in this direction, some of them so far successful as to achieve a limited adoption; and at length a process of reviving the spent manganese residue by effecting its aerial oxidation, has proved a decided commercial success. This process, introduced by Mr. Walter Weldon, has the incidental advantage of doing away with the discharge of the extremely corrosive manganese liquor into streams and watercourses, whereby great damage was frequently occasioned. It consists substantially in neutralizing with chalk, the acid liquor left by the action of the muriatic acid on the manganese, and then pumping air through the neutralized liquor mixed with excess of lime. The original acid liquor is substantially a solution of chloride of manganese with perchloride of iron, chloride of aluminum, chloride of calcium, and the excess of chloride of hydrogen, or muriatic acid, employed. By neutralization of the acid liquor with chalk, the iron of the perchloride of iron is precipitated, and a pale pink manganous solution left. By

treatment of this solution with milk of lime, an almost white precipitate, consisting of hydrated protoxide of manganese with excess of hydrate of lime, is thrown down. Then by blowing air through the resulting thin sludge, raised to the temperature of 140° – 160° F. by injection of steam, oxygen is rapidly absorbed, and the sludge rendered of a deep black colour. By subsidence the now black sludge yields a dense deposit, from which the supernatant clear liquid is run off. Finally, the deposit in its moist condition, and containing in every cubic foot about four pounds weight of peroxide of manganese, is acted upon by muriatic acid in the chlorine stills, and the resulting acid liquid treated over again in the same way, and so on indefinitely.

Already the Weldon process of manganese restoration is employed and about to be employed at many large works, to such an extent that before very long one-half of the entire quantity of bleaching powder produced in the kingdom may be expected to be made with chlorine generated by means of the restored manganese. It is noteworthy that the original pale precipitate of hydrated protoxide of manganese undergoes oxidation very imperfectly save in presence of a considerable excess of lime, and that the black product finally obtained is not simply peroxide of manganese MnO_2 , but a compound of the peroxide with lime, of composition varying in different instances between that indicated by the respective formulæ $\text{CaO} \cdot \text{MnO}_2$ and $\text{CaO} \cdot 2\text{MnO}_2$, a small portion of the lime CaO being usually replaced by its equivalent of protoxide of manganese MnO . Some idea of the rapidity of oxidation effected under favourable circumstances may be gathered from the following result. Of the entire quantity of oxygen contained in 175,000 cubic feet of air blown into the sludge within five hours, 14.8 per cent., equal to rather more than four hundredweights, was absorbed in the production of twenty-two hundredweights of manganese peroxide MnO_2 . It is obvious that where Weldon's process is carried out, what happens is this:—The original peroxide of manganese first oxidizes a quantity of muriatic acid, and sets free its chlorine. Then the spent manganese is caused to acquire a fresh dose of oxygen from the air, and is used to oxidize a fresh quantity of muriatic acid, and so on continuously. Thus, except during the first use of the manganese, the muriatic acid is really oxidized by the oxygen of the air, the manganese serving only as a carrier. Latterly, Mr. H. Deacon, of the Widnes Alkali Works, has conceived the idea of dispensing with the carrier—that is the manganese—altogether. It has been known for some time that when muriatic acid vapour mixed with air is passed through heated tubes, the oxygen of the air effects a partial oxidation of the muriatic acid, setting free its chlorine; but the reaction is not sufficiently complete to render the process commercially available. Mr. Deacon however has ascertained that when a mixture of air and muriatic acid vapour, heated to about 700° F., is passed over a mass of brickwork that has been steeped in solution of sulphate of copper and afterwards dried, an almost complete decomposition of the muriatic acid is effected. The copper salt

certainly takes part in the reaction as an intermediary, but in the end is quite unaffected, the sole obvious result being that the chlorine of the muriatic acid is set free by the oxygen of the air, with a rapidity which seems to leave nothing to be desired. The nature of the intermediary action exerted by the copper-salt, so ingeniously made serviceable by Mr. Deacon, has not been clearly ascertained. It would appear, however, that by two simultaneous reactions taking place continuously throughout the process, chloride of copper is ever being alternately formed and decomposed; it being remembered that chloride of copper gives off a portion of its chlorine with much facility, even by heat alone. The extreme result would probably be somewhat as follows:



Although this new process has not yet been worked on a manufacturing scale, considerable experience has been acquired with regard to it, and the difficulties to which it at first seemed liable have been successfully provided against. One inevitable difficulty arising from the diluted state of the produced chlorine, has proved to be less serious than was anticipated. This state of dilution is at all times considerable; for the chlorine being generated by the action of atmospheric oxygen on muriatic acid, every volume of chlorine produced even in an absolutely perfect working of the process, must be necessarily diluted with twice its volume of atmospheric nitrogen. Nevertheless, according to Mr. Deacon's experience, the diluted state in which the chlorine is always obtained, has not been found to interfere with its application to the manufacture either of chlorate of potash or bleaching powder. The requisite plant for carrying out the invention on a large scale is now being erected at Messrs. Gaskell and Deacon's works.

For experimental purposes the new process of continuous chlorine production may be performed with oxygen instead of air. It then manifests a striking reverse relationship to a process of continuous oxygen production, in which oxide of cobalt acts as a permanent intermediary. In the one experiment the gas goes in oxygen and comes out chlorine, muriatic acid being decomposed and water formed. In the other experiment the gas goes in chlorine and comes out oxygen, water being decomposed and muriatic acid formed. In the presence of slaked lime to arrest the muriatic acid, this last reaction takes place readily and completely below the boiling point of water.

[W. O.]

Friday, February 3, 1871.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

W. SPOTTISWOODE, Esq. M.A. Treas. R.S. and R.I.

*On some Experiments on Successive Polarization of Light made by
Sir C. Wheatstone.*

THE experiments which formed the subject of this discourse were made by Sir Charles Wheatstone some years ago, but the pressure of other avocations delayed their publication. The term "Successive polarization" was applied by Biot to denote the effects produced when a ray of polarized light is transmitted through a plate of rock crystal cut perpendicularly to the axis. The plane of polarization is found to be changed on emergence and through a different angle for each homogeneous ray. The introduction of instrumental means for converting the plane polarization of the ordinary apparatus into successive, or, as it is more commonly called, circular polarization, and the explanation of the phenomena thence arising, constitute the main purpose of the communication.

Polarized light is distinguished from common light by the presence of certain peculiarities not ordinarily found; but the peculiarities in question cannot be discerned by the unassisted eye, and require special instrumental appliances for detection. A simple mode of bringing light into the condition in question is by allowing it to pass through a plate of the crystal called tourmalin, cut parallel to the axis; and if the light be then examined by causing it to pass through a second similar plate, held parallel to the former and caused to revolve like a wheel in its own plane, it will be found that the intensity alternately diminishes and revives, being zero for two positions 180° from one another, and a maximum for two positions at 90° from each of the former. Thus combination of tourmalins constitute in fact a polariscope, which in general consists of two parts, counterparts of each other, the first for bringing common light into the condition in question, in other words for *polarizing*; the second for examining or *analyzing* the light.

The explanation of this fundamental phenomenon is as follows:—The vibrations upon which the sensation of light depends, may in ordinary light take place in any direction in a plane perpendicular to the ray. By the process of polarization they are all brought into one direction, still, however, perpendicular to the ray: so that throughout the entire ray they lie in one plane. On this account the polarization here considered is called plane polarization. There are other kinds

of polarization, such as circular and elliptic, whose names are derived from the curves, or orbits, described by the vibrating particles.

There are also other methods for producing plane polarization beside that above described; *e.g.* reflexion at particular angles from the surfaces of transparent media, transmission through parallel plates of glass, &c.; but as they all agree in reducing common light to the same condition, it is unnecessary for the present purpose to allude to them more in detail.

If a ray of polarized light fall upon a plate of doubly-refracting crystal, it is divided into two, whose vibrations lie in planes perpendicular to one another. These rays traverse the crystal with different velocities, and therefore emerge with a difference of phase. On entering the analyzer the vibrations of both rays are resolved into one plane. If the plane of vibration of the analyzer be parallel to one of those of the crystal, one ray will be cut off, the other will be transmitted without change. In any other position of the analyzer the transmitted portions of the two rays will interfere so as to produce colour; and if the analyzer be then turned through 90° , the portion of the original light cut off in the first position will be transmitted, and *vice versa*.

Of this theory the following are the experimental results:—If a plate of doubly-refracting crystal, *e.g.* selenite, be placed between the polarizer and analyzer, and turned round in its own plane, it will be found that in certain positions at right angles to one another no effect is produced. These may be called neutral positions. In all other positions the field is tinted with colour, which is most brilliant when the plate has been turned through 45° from a neutral position. If the analyzer be turned, the crystal remaining still, the colour will fade, and entirely vanish when the angle of turning amounts to 45° . From this position the complementary colour will begin to appear, and will be brightest when the angle of turning amounts to 90° . The colour depends upon the thickness of the crystal, so that by a suitable preparation any arrangement of colours may be produced.

So far for plane polarization. The principle of circular or successive polarization, as regards the present purpose, is as follows:

If two sets of rectilinear vibrations lying in planes perpendicular to one another meet and combine, the resulting vibration will be curvilinear, whose form and position depends upon the difference of phase of the components. If the second set be in advance or in rear of the first by a quarter of a wave length, the resulting vibration will be circular; but the motion will in one case be direct (like the hands of a watch), in the other it will be reverse.

If two sets of circular vibrations in opposite directions meet and combine, the resulting vibrations will be rectilinear, and the position of its plane will depend upon the difference of phase of the components. If the second set advance upon the first, the plane of resultant vibration will undergo direct rotation; if it recede, it will undergo reverse rotation.

If in such an experiment white light be used, the vibrations of the different component prismatic colours will (on account of their different wave lengths) undergo different retardation; and consequently the resulting vibrations will lie in different planes, arranged in prismatic order. The order will be from red to violet, or *vice versâ*, in accordance with the law stated above.

If a ray of plane polarized light fall upon a metallic reflector, it is divided into two, whose vibrations are respectively parallel and perpendicular to the reflector; and the latter is retarded behind the former by a difference of phase depending upon the angle of incidence. If the plane of vibration of the incident ray be inclined at an angle of 45° to the plane of incidence, the two rays into which it is divided have nearly the same intensity. At an angle, nearly 45° , which varies with the metal employed, but which is perfectly definite, the intensities become accurately equal. And further, if the angle of incidence have a particular value dependent upon the nature of the metal (for silver 72°), the retardation will amount to a quarter of a wave length. These two rays, on leaving the reflector, will recombine, and in accordance with the laws above given, will in the last-mentioned circumstances become a circularly polarized ray. Lastly, the direction of motion in this circular ray will depend upon the side on which the original plane of vibration is inclined to the plane of incidence; if, when it is inclined on one side, the circular ray becomes right-handed, then, when it is inclined on the other, it becomes left-handed.

Reverting then to the phenomena of double refraction produced by a plate of crystal cut parallel to the axis on a plane polarized ray; let the crystal be placed in such a position that the planes of vibration of the two resulting rays are inclined at angles of 45° on the two sides respectively of the plane of incidence; and let there be interposed between the crystal and the analyzer a silver plate at an angle of 72° to the direction of these emergent rays. Each of these rays will, in virtue of the principles enunciated above, be converted by reflexion into a circularly polarized ray; but one will be a right-handed and the other a left-handed ray; and the difference of phase produced by the doubly-refracting plate will be undisturbed by the reflexion. This difference of phase depends, as is well known, upon the wave length, in other words, upon the colour of the light. So that the two circular rays will combine to form a plane polarized ray, whose plane of vibration depends upon the difference of phase, *i. e.* upon its colour. And if, finally, the light be then examined by an analyzer in the usual manner, we shall have all the phenomena of circular or successive polarization.

From what has been stated above, it appears that the direction of motion in the two circular rays, and consequently the order of colours produced, depends upon the position (to the right or left of the plane of incidence) of the ray which has been most retarded in the passage through the crystal plate. If, therefore, the plate being in a given position, the colours appear in an ascending order, then on turning the plate through 90° in its own plane, or on turning it over about an

axis in the plane of incidence, the swifter and the slower rays will change position, and the order of colours will be reversed.

The reversal of the order of colour may be exhibited in another way. Uniaxal crystals are divided into two classes: one, called positive (*e. g.* quartz), in which the extraordinary ray moves more slowly than the ordinary; the other, called negative (*e. g.* Iceland spar), in which the ordinary ray is the slowest. If, therefore, a plate of quartz placed with its axis at 45° on one side of the plane of incidence give the colours in one order, a similar plate of Iceland spar similarly placed will give them in the reverse order.

The same principles apply to the case of biaxal crystals cut parallel to a plane containing the two optic axes. A ray of plane polarized light transmitted through such a plate is divided into two, whose vibrations respectively bisect the angles formed by the two axes; the line which bisects the smallest angle is called the intermediate section, and the line perpendicular to it the supplementary section; and the order of the colours depends upon the relative velocity of the two rays. In selenite the ray whose vibrations lie in the supplementary section is the slowest; in mica it is the swiftest. Hence these two crystals will, all other circumstances being alike, give opposite orders of colour, and may be regarded as positive and negative respectively, like quartz and Iceland spar.

The phenomena by which these principles may be illustrated are very numerous and varied, but are better seen than described.

[W. S.]

Friday, February 24, 1871.

WILLIAM SPOTTISWOODE, Esq. Treasurer R.S. & R.I. and Vice-President,
in the Chair.

W. MATTIEU WILLIAMS, F.C.S.

On Rumford's Scientific Discoveries.

THE speaker ventured to assert that it would be difficult, or even impossible, to name any philosopher, statesman, and philanthropist of equal eminence to Benjamin Thompson, Count of Rumford, concerning whom so little is popularly known. This may be explained by the facts that his statesmanship and philanthropic efforts were chiefly exerted abroad, and that his philosophical researches resulted in scarcely anything admitting of attractive lecture-table illustration, while the discoveries of so many of his contemporaries and immediate successors were most brilliant in this respect.

The electrical machine, the voltaic battery, oxygen, hydrogen, chlorine, the metals of the alkalis, &c., by supplying lecture-table experiments of such marvellous and previously unknown brilliancy, developed a new race of teachers—the popular experimental lecturers, to whom we are mainly indebted for the popular diffusion of scientific knowledge during the present century, and the philosophers whose names are connected with the discovery of the materials which supplied these teachers with their favourite illustrations, are naturally the best known to their pupils.

The researches of Rumford are nevertheless especially worthy of general attention, as his subjects literally come home to all of us, the greater part of his life having been devoted to studying and applying the philosophy of common things; he may be, in fact, regarded above all others as the philosopher of common things, the science of feeding, clothing, warming, and sheltering of mankind having been his chief pursuit, as the following list of the subjects of his essays and researches will show.

The Force of Fired Gunpowder.—Improvements in Field Artillery and Guns generally.—Naval Architecture.—Naval Signals (the essays on these two last-named subjects have not yet been published).—The Transmission of Heat through Solids, Liquids, Gases, and Vacuo.—The Relative Warmth of Different Materials used for Clothing.—The Quantities of Moisture absorbed from the Atmosphere by Different Materials used for Clothing.—The Production of Air from Water.—Photometry. Coloured Shadows.—The Harmony of Colours.—The Chemical Properties which have been attributed to Light.—

The Weight or Ponderability ascribed to Heat.—The Suppression of Mendicity, and the Economical Clothing, Feeding, Housing, and Industrial Education of the Poor.—The Philosophy and Practice of Cookery.—The Nutritive Value of Different Kinds of Food.—The Cultivation and Use of the Potato.—The Construction of Stoves and Open Fireplaces.—The Curing of Smoky Chimneys.—The Organization of Military Academies.—General Military Organization.—The Education and the Civil Utilizing of the Soldier.—The Economy of Fuel.—The Construction of Kitchen Furnaces—of Boilers—Roasters—Saucepans—Stewpans—Gridirons—Dripping-pans—Ironing Stoves—Cottage Fireplaces—Steam Stoves—Limekilns—Ovens—Teakettles—Steam Cooking Apparatus—Dye-house Vats—Distillers' Coppers—Drying-houses—Laundries—Lamps, Safety-valves, &c.—The Preparation of Cheap Soups, Indian Puddings, Macaroni, Potato Salads, Potato Dumplings, &c.—The Internal Movements of the Particles of Heated Fluids.—The Final Cause of the Saltiness of the Sea.—The Influence of Water in Equalizing Climate.—The Heating of Buildings by Steam.—The Boiling of Water and various Solutions by the Latent Heat of Steam.—The Salubrity of Warm Bathing (an Essay advocating the introduction of the Turkish Bath).—The Pleasure of Eating, and the Means that may be employed for Increasing it.—The Tensile Strength of Different Substances.—The Suppression of Usury in Bavaria.—The Improvement of the Breed of Horses and Horned Cattle in Bavaria.—The Relative Heating Power of Coal and Different Kinds of Wood.—The Source of Heat excited by Friction.

This list is mainly made up of practical subjects, on which Count Rumford did not merely write suggestive or speculative essays, but which he dealt with practically by carrying out successfully on a practical scale his suggestions and improvements. All his practical successes were effected by the application of scientific principles, Rumford's method invariably being to set before himself the task to be performed, then to determine the philosophical principles involved and having done this, to apply these principles practically. Most of his purely philosophical investigations were suggested by demands thus practically created, or by phenomena observed in the course of his practical work.

The great characteristic of Rumford's whole career is that *all* his practical work was strictly philosophical, and most of his philosophical work was eminently and directly practical.

When, for example, he was commissioned by the Elector of Bavaria to reorganize the Bavarian army, he studied the philosophy of cookery, and made experiments upon the nutritive value of different kinds of food, in order that he might feed the men as well and as economically as possible. His improvements in stoves, kitchen utensils, &c., his numerous researches and essays on subjects connected with the general economy of the kitchen and the preparation of food, are the results of his thorough and philosophical method of solving this very practical problem. The barrack requirements led him to study further the

economy of fuel in the warming of dwellings, the construction of heating and ventilating apparatus, and of buildings generally.

In order to determine the best material for the soldier's clothing, he first considered the function of clothing, and determined that in winter it should act by resisting the transmission of the animal heat to the cooler atmosphere, and thereby maintain the body at the temperature required; that for this purpose a non-conductor or a bad conductor of heat is required. The relative conducting power of different clothing materials being in his time unknown, he constructed a theoretical soldier in the form of a thermometer, which he could clothe with the materials to be tested. By heating this clothed thermometer, and allowing it to cool in an apartment of constant temperature, he obtained the following results:—

Thermometer sur- rounded by	Air	{ cooled from 70° to 10 (Réaumur) }	in 576 seconds.
"	16 grs. of Fine lint	" "	1032 "
"	" Cotton wool	" "	1045 "
"	" Sheep's wool	" "	1118 "
"	" Raw silk	" "	1284 "
"	" Beaver's fur	" "	1296 "
"	" Eider-down	" "	1305 "
"	" Hare's fur	" "	1315 "

Finding that the raw silk only occupied $\frac{1}{5}$ th of the whole bulk of the outer bulb containing it, he calculated that if it were an absolute non-conductor, it should, as compared with the envelop of air contained in the same space, only increase the resistance by ten seconds, but the experiment showed that it had above seventy times the effect. Therefore the resistance of the silk fibre cannot account for the result. Connecting this with his previous investigations on the convection of heat by liquids, Rumford inferred that air is a non-conductor of heat, that the fibres acted by enclosing the air between them, and preventing those convection movements by which alone it can carry heat away from a body in contact with it. He confirmed this explanation by a series of experiments. He found that when the thermometer was surrounded by the same quantity of the above-named materials more closely twisted or woven, so as to leave less air space between the fibres, their power of resisting the passage of heat was diminished proportionately to the closeness of the weaving, or twisting, or packing.

He thus not only solved his practical question of clothing, but made important discoveries respecting the laws of transmission of heat by gases, and further applied these to retaining heat in furnaces and buildings by means of cellular walls, or double walls and windows.

The question of what is the best material for summer clothing was decided in like manner. He first considered how the body retains its temperature when exposed to direct summer sunshine in hot climates, or otherwise, when a thermometer similarly exposed rises above blood heat. He concluded that it is by the evaporation of the insensible perspiration. How, then, may clothing aid this? Evidently by

its power of absorbing the aqueous vapour. Do clothing materials thus absorb vapour? If so, do they differ in their powers of absorption?

To answer these questions he exposed the following substances, carefully cleaned, upon china plates for twenty-four hours, in a room that had for several months been dried by a German stove, its atmosphere having for six hours previous to the experiment been raised to 85° Fahr. After this exposure 1000 parts of each were weighed in the dry room; then this quantity was exposed for forty-eight hours in an uninhabited room and weighed again; then for seventy-two hours in a very damp cellar. The results were as follows:—

1000 Parts of		After 48 hours in room, weighed	After 74 hours in cellar, weighed
Sheep's wool	1084	1163
Beaver's fur	1072	1125
Fur of Russian hare	1065	1115
Eider-down	1067	1112
Silk	Raw	1057	1107
	Ravellings of white taffety ..	1054	1103
Linen	Fine lint	1046	1102
	Ravellings of fine linen ..	1044	1082
Cotton wool	1043	1089
Silver wire—Ravellings of gold lace	..	1000	1000

From these and other experiments he concluded that light flannel is the best clothing for summer, and he strongly advocates its universal adoption. The soundness of his conclusion is confirmed by the subsequent experience both of soldiers and sailors, and of cricketers, rowers, furnace-men, and all who are engaged in work that induces much perspiration.

Count Rumford's researches and inventions connected with his greatest subject, that of cookery, afford abundant examples of his applications of philosophy to practical affairs; but the extent of the subject forbids the citation of more than one small characteristic sample. After advocating the extended use of Indian corn and giving general directions for its use, and particularly for the preparation and cooking of "Indian pudding," including the scientific manipulation of the pudding bag, he concludes as follows:—"The pudding is to be eaten with a knife and fork, beginning at the circumference of the slice and approaching regularly towards the centre, each piece of pudding being taken up with the fork and dipped into the butter, or dipped in *part only*, as is commonly the case, before it is carried to the mouth."

Again in his essay "On the Pleasure of Eating and the Means that may be employed for increasing it," after showing that the pleasure of eating is produced by bringing the surface of the food in contact with the surface of the tongue and the palate, and how a given quantity of food may have its contact surface increased, he says in apology for his subject, "If a glutton can be made to gormandize

two hours upon two ounces of meat, it is certainly better for him than to give himself an indigestion by eating two pounds in the same time."

As an example of his theoretical work his speculations on the movements of the molecules of a heated fluid may be cited. He supposes the case of a coin or pebble at the bottom of an open vessel of water, and says, "As a ray of light cannot fail to generate heat when and where it is stopped and absorbed, the rays which, entering the water and passing through it, impinge against the small solid opaque body at the bottom of the vessel are there absorbed, and must necessarily generate a certain quantity of heat; a part of which will be communicated to those colder particles of water which repose on its surface."

He had already shown by a series of very simple and conclusive experiments that the particles of a fluid thus heated are set in *visible* motion, and he supposes the case of a molecule of water in contact with the coin, and having a diameter of $\frac{1}{1000000}$ th of an inch to move at the least rate of visible motion $\frac{1}{100}$ th of an inch per second. Thus it will move through 10,000 times its own diameter in a second. Taking the greatest velocity of a 9-pounder cannon ball, 4 inches in diameter, at 1600 feet per second, it passes through only 4800 diameters per second; thus the *relative* velocity of the molecule of water is more than double that of the cannon ball. Such a molecule thus moving will come in contact with at least 600,000 others per second, to each of which it will impart a portion of its heat and motion. Thus, every inequality of temperature induces violent molecular agitation, and Rumford asks whether animal life may not depend upon such motion, seeing that the organic apparatus is mainly fluid, or fluids contained between walls and in channels, and that there is a continual internal heating and external cooling due to respiration and surface evaporation and radiation, or in his own words: "Do not respiration, digestion, and insensible perspiration all tend evidently (that is to say, according to our assumed principles with regard to the manner in which heat is propagated in fluids) to *produce* and to *perpetuate* this inequality of heat in the animal fluids. And do we not see what an immediate and powerful effect they have in increasing the intensity of the action of the powers of life?"

Intimately connected with this essay is another, which appears to be worthy of more attention than it has received, especially in connection with the modern growth of our knowledge of the transmission of light and heat in gases and liquids, and the conversion of one force into another. The title of this essay is "An Inquiry concerning the Chemical Properties that have been attributed to Light." Rumford made a number of experiments upon compounds of gold and silver, by which he showed that the decompositions usually attributed to light could all be effected in precisely the same manner and degree by obscure heat, a temperature below the boiling point of water being sufficient when the salts were in aqueous solution, or a higher tem

perature when the dry salts were used. Also that clear solutions of chloride of gold or nitrate of silver are not decomposed by sunlight unless some body capable of absorbing the light, and thereby converting it into heat, is immersed in them. He asks what is the temperature induced upon the absolute surface of such a light-absorbing body at the instant of absorption or conversion of light into heat. He thinks that it must far exceed that indicated by any form of thermometer, because the thermometer only shows the *mean* temperature of the whole mass of the contents of its bulb, and its absolute surface is perpetually parting with its heat by conduction, radiation, and the convection of the surrounding medium. If the single molecule of water above referred to comes in contact with 600,000 others in the course of a second, and communicates some of its heat to each, we cannot ascertain its initial maximum temperature, and even this is below that of the surface of the coin or pebble from which it received its heat by contact.

The time did not permit the speaker to develop these speculations and connect them with modern philosophy as intended, and he therefore passed on to Rumford's celebrated experiments on "The Source of Heat excited by Friction."

These experiments are so well known that it is unnecessary to repeat their details here. It will be remembered that after taking every precaution to insulate his apparatus from any communication of heat from without, and ascertaining that the specific heat of the borings was unchanged, Rumford found that the heat evolved by the friction of a blunt borer against the inside of a metal cylinder was sufficient to boil 18.77 lbs. of water in 2½ hours, and to keep it boiling as long as the friction was sustained. His own conclusion is thus expressed: "It is hardly necessary to add that anything which an insulated body, or system of bodies, can continue to furnish *without limitation* cannot possibly be a *material substance*; and it appears to me extremely difficult, if not quite impossible, to form any distinct idea of anything capable of being excited and communicated in these experiments except it be MOTION."

The italics and capitals are Count Rumford's. As Dr. Tyndall says, "Rumford in this memoir annihilates the material theory of Heat. Nothing more powerful on the subject has since been written," and "hardly anything more conclusive has since been adduced in the way of establishing that Heat is what Rumford considered it to be—'*MOTION*.'"

This memoir, and the one immediately connected with it, "On the Weight or Ponderability ascribed to Heat," and his investigations on the Transmission of Heat through Gases and Liquids, are perhaps the most important of Rumford's purely philosophical works, and he is the father of the Royal Institution. All who have followed the recent progress of physical science must admit that this Institution has been a dutiful child and has worthily cultivated its patrimonial inheritance.

Old-fashioned story-tellers were wont to conclude their discourse with a "moral." This old fashion may be profitably followed in the present instance, when we remember that Benjamin Thompson began life in extreme poverty, was a poor teacher in a poor colonial village school, that step by step he rose to such honour and distinction, that when Bavaria was so sorely threatened that its sovereign was obliged to fly from Munich, full powers of temporary sovereignty were placed in Rumford's hands, and he wielded this power with complete success. He practically solved great social problems and achieved great social reforms, such as to this day, after a lapse of above seventy years, we all desire to see repeated, and yet cannot achieve again. He abolished mendicity from a country where it prevailed to an almost unprecedented extent; he succeeded in making the rogues and vagabonds of Bavaria pay all the expenses of their food, clothing, and lodging, and leave a handsome balance towards the maintenance of the police who apprehended them. He thus provided for the poor of an excessively pauperized country without any poor's-rates. He was a great statesman, a practical soldier, the greatest of practical military reformers, a skilful mechanic and engineer, and a successful philanthropist, besides being a distinguished philosopher. All his success is clearly traceable to the fact that whatever he did, from the eating of a slice of pudding to the dictatorship of a nation, was done by rigidly obeying those principles of inductive reasoning which have led to the marvellous triumphs of modern science.

If, therefore, you would make your son a successful soldier, a successful lawyer, a successful statesman, successful in any business or profession whatever, you should give him a sound, practical scientific education; let him learn how to observe and investigate facts, to generalize them, and from such inductions to deduce sound rules for practical conduct.

Modern science affords the best, the highest, and the most useful school of intellectual culture: the great business of the present day is to give to science that decided educational precedence to which it is entitled, and the whole career of Benjamin Thompson, Count Rumford, affords a striking example of the kind of intellectual results we may expect to obtain when sound scientific knowledge and training are afforded to every human being—male and female.

[W. M. W.]

Friday, April 28, 1871.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, M.B. F.R.S.

FULLERIAN PROFESSOR OF CHEMISTRY, ROYAL INSTITUTION.

On the Revived Theory of Phlogiston.

Observationem, quam produco, bono jure mihi vindico. . . . Materia hæc ignescens, in omnibus tribus regnis, una eademque existit. Unde, ut e vegetabili in animale, abundantissime transmigrat, ita ex utrolibet horum, in mineralia et ipsa metalla, promptissime omnium transfertur.—STAHLII, Experimenta, Observationes, Animadversiones, CCC Numero.

IN 1781–83, Cavendish showed that when inflammable air or hydrogen, and dephlogisticated air or oxygen, are exploded together in certain proportions, “almost the whole of the inflammable and dephlogisticated air is converted into pure water,” or as he elsewhere expresses it, “is turned into water.”

On June 24, 1783, the experiment of Cavendish was repeated on a larger scale and in a somewhat different form by Lavoisier, who not only confirmed the synthesis of the English chemist, but drew from it the conclusion—at first strongly contested, then rapidly acknowledged, and since never called into question—“that water consists of inflammable air united to dephlogisticated air,” or that it is a compound of hydrogen and oxygen.

This conclusion, so opposite to his own preconception on the matter, Lavoisier subsequently confirmed by an analysis of water. He found that iron, heated to redness and exposed to the action of water-vapour, became changed by an abstraction of oxygen from the water, into the self-same oxide of iron procurable by burning the metal in oxygen gas,—the other constituent of the water, namely, its hydrogen, being freely liberated.

With the demonstration by Lavoisier of the composition of water began the triumph of that antiphlogistic theory, which he had conceived, in a necessarily imperfect form, so far back as 1772, or before the discovery of oxygen, and had brought to completion by the aid of every successive step in pneumatic chemistry, achieved by himself or by others.

In 1785, the relationship to one another of hydrogen and water being then conclusively established, Berthollet declared himself a convert to the new theory of combustion put forward by his countryman. Fourcroy next gave in his adhesion; and soon afterwards De

Morveau, invited to Paris expressly to be reasoned with by Lavoisier, succumbed to the reasons set before him. The four chemists then associated themselves together, and in spite of a strong though short-lived opposition both in England and Germany, succeeded in obtaining for *La Chimie Française* an all but universal recognition.

The principal articles of the new or antiphlogistic theory of combustion propounded by Lavoisier are as follows:—That combustible bodies in burning yield products of various kinds,—solid in the case of phosphorus and the metals, liquid in the case of hydrogen, gaseous in the case of carbon and sulphur. That in every case the weight of the products formed by the burning is greater than the weight of the combustible burnt. That the increase of weight is due to an addition of matter furnished to the combustible by the air in which its burning takes place. That bodies of which the weights are made up of the weights of two or more distinct kinds of matter are of necessity compound; whereas bodies of which the weights cannot be shown to be made up of the weights of two or more distinct kinds of matter are in effect simple or elementary. That inasmuch as the weights of the products furnished by the burning of different combustibles are made up of the weights of the combustible burnt and of the oxygen consumed in the burning, these products are compound bodies—oxides in fact of the substances burnt. That inasmuch as given weights of many combustibles, as of hydrogen, sulphur, phosphorus, carbon, and the metals, are not apparently made up of the weights of two or more distinct kinds of matter, these particular combustibles are in effect elementary; as for the same reason is the oxygen with which in the act of burning they enter into combination. And, lastly, that combustion or burning consists in nothing else than in the union of combustible matter, simple or compound, with the empyreal matter, oxygen—the act of union being somehow attended by an evolution of light and heat. And except that it would be necessary nowadays to explain how in certain cases of combustion, the combustible enters into union not with oxygen, but with some analogue of oxygen, the above precise statement might equally well have been made by Lavoisier in 1785, or be made by one of ourselves at the present day.

Lavoisier's theory of combustion being known as the antiphlogistic theory, the question arises, What was the phlogistic theory to which it was opposed, and which it succeeded so completely in displacing? This phlogistic theory was founded and elaborated at the close of the seventeenth century by two German physicians, Becher and Stahl. Having exercised a scarcely disputed authority over men's minds until the notorious defection in 1785, it preserved for some years longer a resolute though tortuous existence, and was to the last defended and approved by our own Priestley and Cavendish—who died the former in 1804, and the latter in 1810.

The importance attached to the refutation of this theory may be judged of from the circumstance that after the early experiments of Lavoisier on the composition and decomposition of water had been

successfully repeated by a committee of the French Academy in 1790, a congratulatory meeting was held in Paris, at which Madame Lavoisier, attired as a priestess, burned on an altar Stahl's celebrated *Fundamenta Chemicæ Dogmaticæ et Experimentalis*, solemn music playing a requiem the while. And the sort of estimation in which the Stahlian doctrines have since been held by chemists is fairly illustrated by a criticism of Sir J. Herschel, who, speaking of the phlogistic theory of chemistry, says that it "impeded the progress of the science, as far as a science of experiment can be impeded by a false theory, . . . by involving the subject in a mist of visionary and hypothetical causes in place of the true acting principles." Possibly, however, this much-abused theory may yet prove to contain an element of permanent vitality and truth; anyhow the study of this earliest and most enduring of chemical theories can never be wholly devoid of interest to chemists.

To appreciate the merit of the phlogistic theory it is necessary to bear in mind the period of its announcement. Its originator, Beccher, was born in 1625, and died a middle-aged but worn-out man in 1682, a few years before the publication of the 'Principia.' His more fortunate disciple, Stahl, who was born in 1660 and died in 1734, in his seventy-fifth year, though afforded a possibility of knowing, seems equally with Beccher to have remained throughout his long career indifferent to the Newtonian principle that the weight of a body is proportionate to its quantity of matter—that loss of weight implies of necessity abstraction of matter, and increase of weight addition of matter. Whether or not the founders of the phlogistic theory conceived that change of matter in the way of kind, might equally with its change in point of quantity, be associated with an alteration in weight—and it must not be forgotten what pains Newton thought it necessary to take in order to show the contrary—certain it is they attached very little importance to the changes of weight manifested by bodies undergoing the metamorphosis of combustion. It might be that when combustible charcoal was burned the weight of incombustible residue was less than the original weight of charcoal—it might be that when combustible lead was burned the weight of incombustible residue was greater than the original weight of metal—this was far too trifling an unlikeness to stand in the way of the paramount likeness presented by the two bodies. For the lead and charcoal had the common property of manifesting the wonderful energy of fire; they could alike suffer a loss of light and heat—that is, of phlogiston—by the deprivation of which they were alike changed into greater or less weights of inert incombustible residue.

And not only were these primitive students of the philosophy of combustion unconscious of the fact and meaning of the relationship in weight subsisting between the consuming and the consumed body, but they were altogether ignorant of the part played by the air in the phenomena which they so boldly and successfully attempted to explain. Torricelli's invention of the barometer and Guericke's invention of the

air-pump were both indeed made during Beccher's early boyhood ; but years had to elapse before the consequent idea of the materiality of air could be domiciled, as it were, in human understandings. And not until more than a century after Torricelli's discovery of the weight of air,—not, indeed, until the time of the great pneumatic chemists Black, and Cavendish, and Priestley, and Scheele, was it ever imagined that the aerial state, like the solid or liquid state, was a state common to many distinct kinds of matter ; and that the weight or substance of a rigid solid might be largely contributed to by the weight or substance of some constituent having its independent existence in the aerial or gaseous form. The notion that 100 lbs. of smithy-scales might consist of 73 lbs. of iron and 27 lbs. of a particular kind of air, and that 100 lbs. of marble might consist of 56 lbs. of lime and 44 lbs. of another kind of air, was a notion utterly foreign to the older philosophy. Air, it was allowed, might be rendered mephitic by one kind of contamination, and sulphurous by another, and inflammable by a third ; it might even be absorbed in, and so add to the weight of, a porous solid, as water is absorbable by sand ; but still air was ever indisputably air, essentially alike and unalterable in its mechanical and chemical oneness. This familiar conception had to be overcome, and the utterly strange notion of the largely aerial constitution of solid matter to be established in its stead, by the early pneumatic chemists, Black, and Cavendish, and Bergmann, before the deficiencies rather than positive errors of the phlogistic theory could be perceived.

But long ere the foundation of modern chemistry had thus been laid, in 1756, by Black's discovery of fixed air or carbonic acid as a constituent of mild alkalis and limestone, those old German doctors, Beccher and Stahl, though ignorant of the nature of air and neglectful of the import of gravity, had yet found something to say about the chemistry of combustion worthy of being defended a century afterwards by men like Priestley and Cavendish,—worthy, it is believed, of being recognized nearly two centuries afterwards as the expression of a fundamental doctrine in chemical and cosmical philosophy. They pointed out, for example, that the different and seemingly unlike processes of burning, smouldering, calcining, rusting, and decaying, by which combustible is changed into incombustible matter, have a community of character ; that combustible bodies possess in common a power or energy capable of being elicited and used, whereas incombustible bodies are devoid of any such energy or power ; and lastly, that the energy pertaining to combustible bodies is the same in all of them, and capable of being transferred from the combustible body which has it to an incombustible body which has it not, rendering the body that was energetic and combustible inert and incombustible, and the body that was inert and incombustible energetic and combustible—and further rendering some particular body combustible over and over again. That this is a fair representation of the views held by phlogistic chemists is readily recognizable by a study of chemical works written before the outbreak of the antiphlogistic revolution. After

Lavoisier's challenge, the advocates of phlogiston, striving to make it account for a novel order of facts with which it had little or nothing to do, were driven to the most incongruous of positions; for while Priestley wrote of inert nitrogen as phlogisticated air, Kirwan and others regarded inflammable hydrogen as being phlogiston itself in the isolated state. Very different is the view of phlogiston to be gathered from the writings of Dr. Watson, for example, who was appointed Professor of Chemistry at Cambridge in 1764, became Regius Professor of Divinity in 1771, and Bishop of Llandaff in 1782. This cultivated divine, indifferent it is true to the novel questions by which in less placid regions men's minds were so deeply stirred, amused the leisure of his dignified University life by writing scholarly accounts of the chemistry it had formerly been his province to teach; and in the first volume of his well-known 'Chemical Essays,' published in 1781, the following excellent account of phlogiston is to be found:—

"Notwithstanding all that perhaps can be said upon this subject, I am sensible the reader will still be ready to ask, *What is phlogiston?* You do not surely expect that chemistry should be able to present you with a handful of phlogiston, separated from an inflammable body; you may just as reasonably demand a handful of magnetism, gravity, or electricity to be extracted from a magnetic, weighty, or electric body. There are powers in nature which cannot otherwise become the objects of sense, than by the effects they produce; and of this kind is phlogiston. But the following experiments will tend to render this perplexed subject somewhat more clear.

"If you take a piece of *sulphur* and set it on fire, it will burn entirely away, without leaving any ashes or yielding any soot. During the burning of the sulphur, a copious vapour, powerfully affecting the organs of sight and smell, is dispersed. Means have been invented for collecting this vapour, and it is found to be a very strong acid. The acid thus procured from the burning of sulphur, is incapable of being either burned by itself, or of contributing towards the support of fire in other bodies: the sulphur, from which it was procured was capable of both: there is a remarkable difference, then, between the acid procured from the sulphur, and the sulphur itself. The acid cannot be the only constituent part of sulphur; it is evident that *something* else must have entered into its composition, by which it was rendered capable of combustion. This something is, from its most remarkable property, that of rendering a body combustible, properly enough denominated the food of fire, the *inflammable principle, the phlogiston*. . . . This inflammable principle, or phlogiston, is not one thing in animals, another in vegetables, another in minerals; it is absolutely the same in them all. . . . This identity of phlogiston may be proved from a variety of decisive experiments; I will select a few, which may at the same time confirm what has been advanced concerning the constituent parts of sulphur.

"From the analysis or decomposition of sulphur effected by burning,

we have concluded that the constituent parts of sulphur are two—an *acid* which may be collected, and an *inflammable principle* which is dispersed. If the reader has yet acquired any real taste for chemical truths, he will wish to see this analysis confirmed by synthesis; that is, in common language, he will wish to see sulphur actually made by combining its acid with an inflammable principle. It seldom happens that chemists can reproduce the original bodies, though they combine together all the principles into which they have analyzed them; . . . in the instance, however, before us, the reproduction of the original substance will be found complete.

“As the inflammable principle cannot be obtained in a palpable form separate from all other bodies, the only method by which we can attempt to unite it with the acid of sulphur must be by presenting to that acid some substance in which it is contained. Charcoal is such a substance; and by distilling powdered charcoal and the acid of sulphur together, we can procure a true yellow sulphur, in nowise to be distinguished from common sulphur. This sulphur is formed from the union of the acid with the phlogiston of the charcoal; and the charcoal may by this means be so entirely robbed of its phlogiston, that it will be reduced to ashes, as if it had been burned. . . .

“I will in this place, by way of further illustration of the term phlogiston, add a word or two concerning the necessity of its union with a metallic earth, in order to constitute a metal. Lead, it has been observed, when melted in a strong fire, burns away like rotten wood; all its properties as a metal are destroyed, and it is reduced to ashes. If you expose the ashes of lead to a strong fire, they will melt; but the melted substance will not be a *metal*, it will be a yellow or orange-coloured *glass*. If you pound the glass, and mix it with charcoal dust, or if you mix the ashes of the lead with charcoal dust, and expose either mixture to a melting heat, you will obtain, not a *glass*, but a *metal*, in weight, colour, consistency, and every other property the same as lead. The ashes of lead melted *without* charcoal become *glass*; the ashes of lead melted *with* charcoal become a *metal*. The charcoal, then, must have communicated *something* to the ashes of lead, by which they are changed from a glass to a metal. Charcoal consists of but two things—of ashes and of phlogiston; the ashes of charcoal, though united with the ashes of lead, would only produce glass; it must therefore be the other constituent part of charcoal, or phlogiston, which is communicated to the ashes of lead, and by an union with which the ashes are restored to their metallic form. The ashes of lead can never be restored to their metallic form without their being united with *some* matter containing phlogiston, and they may be reduced to their metallic form by being united with *any* substance containing phlogiston in a proper state, whether that substance be derived from the animal, vegetable, or mineral kingdom; and thence we conclude not only that phlogiston is a necessary part of a metal, but that phlogiston has an identity belonging to it, from whatever substance in nature it be extracted. And this assertion still becomes

more general, if we may believe that metallic ashes have been reduced to their metallic form, both by the solar rays and the electrical fire."

The foregoing account by Dr. Watson is almost a translation from Stahl's '*Zymotechnica Fundamentalis, simulque experimentum novum sulphur verum arte producendi*,' in which he establishes what may be called the permanency of chemical substance—that metallic lead is reproducible from the ashes of lead, *sulphur verum* from the acid of sulphur. And, whether or not taking note of the oxidations and deoxidations effected, how little differently, even at the present day, would the actions referred to be described and explained. Is it not our habit to say that charcoal and sulphur and lead are bodies possessing potential chemical energy, that is phlogiston; that in the act of burning, their energy which was potential becomes kinetic or dynamical, and is dissipated in the form of light and heat; that the products of their burning (including the gaseous product now known to be furnished by the burning of charcoal) are substances devoid of chemical energy, that is, of phlogiston; that when the acid substance furnished by burning sulphur is heated with charcoal, some energy of the unburnt charcoal is transferred to the burnt sulphur, just as some energy of a raised weight may be transferred to a fallen one, whereby the burnt sulphur is unburnt, provided with energy, and enabled to burn again, and the fallen weight is lifted up, provided with energy, and enabled to fall again; that the potential chemical energy of metallic lead did not originate in the lead, but is energy or phlogiston transferred thereto from the charcoal by which it was smelted; and lastly, that the chemical energy of the charcoal itself, its capability of burning, its power of doing work, in one word its phlogiston, is merely a portion of energy appropriated directly from the solar rays?

If this be a correct interpretation of the phlogistic doctrine, it is evident that the Stahlans, though ignorant of much that has since become known, were nevertheless cognisant of much that became afterwards forgotten. For most of what has since become known, mankind are indebted to the surpassing genius of Lavoisier; but the truth which he established, alike with that which he subverted, is now recognizable as a partial truth only; and the merit of his generalization is now perceived to consist in its addition to—its demerit to consist in its supersession of—the not less grand generalization established by his scarcely remembered predecessors. This being so, the relationship to one another of the Stahlian and Lavoisierian theories of combustion furnishes an apt illustration of the general truth set forth by a great modern writer, that "in the human mind, one-sidedness has always been the rule, and many-sidedness the exception. Hence, even in revolutions of opinion, one part of the truth usually sets while another rises. Even progress, which ought to superadd, for the most part only substitutes one partial and incomplete truth for another; improvement consisting chiefly in this, that the new fragment of truth is more wanted, more adapted to the needs of the time, than that which it displaces."

The partial truth contributed by Lavoisier was indeed more wanted, more adapted to the needs of the time, than the partial truth which it displaced. To him chemists are indebted for their present conception of material *elements*; and especially for their knowledge of the part played by the air in the phenomena of combustion, whereby oxygenated *compounds* are produced. The phlogistians, indeed, were not unaware of the necessity of air to combustion, but being ignorant of the nature of air were necessarily ignorant of the function which it fulfilled. To burn and to throw off phlogiston being with them synonymous expressions, the air was conceived to act by somehow or other enabling the combustible to throw its phlogiston off; and a current of air was conceived to promote combustion by enabling the combustible to throw its phlogiston off more easily. Moreover, contact of air was not essential to combustion, provided there was present instead some substance, such as nitre, which equally with, or even more effectively than air, could enable the combustible to discharge itself of phlogiston. But while the phlogistians, on the one hand, were unaware that the burnt product differed from the original combustible otherwise than as ice differs from water, by loss of energy; Lavoisier, on the other hand, disregarded the notion of energy, and showed that the burnt product included not only the stuff of the combustible, but also the stuff of the oxygen it had absorbed in the burning. But, as well observed by Dr. Crum-Brown, we now know "that no compound contains the substances from which it was produced, but that it contains them *minus* something. We now know what this something is, and can give it the more appropriate name of potential energy; but there can be no doubt that this is what the chemists of the seventeenth century meant when they spoke of phlogiston."

Accordingly, the phlogistic and antiphlogistic views are in reality complementary and not, as suggested by their names and usually maintained, antagonistic to one another. It has been said, for example, that according to Stahl, the product of combustion is simple, and the combustible a compound of the product with imaginary phlogiston—which is false; whereas, according to Lavoisier, the combustible is simple, and the product a compound of the combustible with actual oxygen—which is true. But in this case, as in so many others, everything turns upon the use of the same word in a different sense at different periods of time. When Lavoisier spoke of red lead as being metallic lead combined with oxygen, he meant that the matter or stuff of the red lead consisted of the matter or stuff of lead *plus* the matter or stuff of oxygen. But when the Stahlians spoke of metallic lead being burnt lead combined with phlogiston, they had the same sort of idea of combination in this instance, as others have expressed by saying that the weight of a body is compounded of its matter and its gravity; or that steam is a compound of water and heat; or, to use a yet more Lavoisierian expression, that oxygen gas itself is a compound of the basis of oxygen with caloric. It is not, then, that the one state-

ment, Stahlian or Lavoisierian, is false and the other true, but that both of them are distorted, because incomplete. Chemists nowadays are both Stahlian and Lavoisierian in their notions; or have regard both to energy and matter. But Lavoisierian ideas still interfere very little with our use of the Stahlian language. While we acknowledge that in the act of burning the combustible and the oxygen take equal part, just as in the act of falling the weight and the earth take equal part, yet in our common language we alike disregard the abundant atmosphere and abundant earth as being necessarily understood, and speak only of the energy of the combustible and of the weight, which burn and fall respectively. Whatever may be the fault of language, however, chemists do not omit to superpose the Lavoisierian on the Stahlian notion. They recognize fully that it is by the union of the combustible with oxygen that phlogiston is dissipated in the form of heat; and further, that phlogiston can only be restored to the burnt combustible on condition of separating the combustible from the oxygen with which it has united; just as energy of position can only be restored to a fallen weight on condition of separating it to a distance from the surface on which it has fallen.

That Stahl and his followers regarded phlogiston as a material substance, if they did so regard it, should interfere no more with our recognition of the merit due to their doctrine, than the circumstance of Black and Lavoisier regarding caloric as a material substance, if they did so regard it, should interfere with our recognition of the merit due to the doctrine of latent heat. But though defining phlogiston as the principle or matter of fire, it is not at all clear that the phlogistians considered this matter of fire as constituting a real body or ponderable substance; but rather that they thought and spoke of it as many philosophers nowadays think and speak of the electric fluid and luminiferous ether. The nondescript character, properly ascribable to phlogiston, is indicated by the following quotation taken from Macquer's '*Elémens de Chymie Théorique*:' 1749. It must not, of course, be forgotten that the popular impression as to phlogiston having been conceived by its advocates as a material substance having a negative weight or levity, is erroneous; and is based on an innovation that was introduced during the struggling decadence of the phlogistic theory, and advocated more particularly by Lavoisier's subsequent colleague, Guyton de Morveau, in his '*Dissertation sur le Phlogistique, considéré comme Corps grave, et par rapport aux changemens de pesanteur qu'il produit dans les corps auxquels il est uni*:' 1762. Macquer writes as follows:—

"La matière du soleil, ou de la lumière, le phlogistique, le feu, le soufre principe, la matière inflammable, sont tous les noms par lesquels on a coutume de désigner l'élément du Feu. Mais il paroît qu'on n'a pas fait une distinction assez exacte . . . du nom qu'il mérito véritablement lorsqu'il entre effectivement comme principe dans la composition d'un corps, ou bien lorsqu'il est seul et dans son état naturel. Si on l'envisage sous cette dernière vue, le nom de Feu, de matière du

soleil, de la lumière et de la chaleur, lui convient particulièrement. Pour lors, c'est une substance que l'on peut considérer comme composée de particules infiniment petites, qui sont agitées par un mouvement très rapide et continu, par conséquent essentiellement fluide. Cette substance, dont le soleil est comme le réservoir général, s'en émane perpétuellement, et est répandue universellement dans tous les corps que nous connoissons ; mais non pas comme principe ou essentielle à leur mixtion, puisqu'on peut les en priver, du moins en grande partie, sans qu'ils souffrent pour cela la moindre décomposition. Cependant les phénomènes que présentent les matières inflammables lorsqu'elles brûlent, nous indiquent qu'elles contiennent réellement la matière du feu comme un de leurs principes. Examinons donc les propriétés de ce feu fixé, et devenu principe des corps. C'est lui auquel nous donnerons particulièrement le nom de matière inflammable, du soufre principe, ou de Phlogistique, pour le distinguer du feu pur."

Again, much the same thing is to be found in Baumé's 'Manuel de Chymie:' 1765 ; as for example :—

"Nous considérons le feu sous deux états différens. Lorsqu'il est pur, isolé, et qu'il ne fait partie d'aucun composé Lorsqu'il est combiné avec d'autres substances, et qu'il fait un des principes constituans des corps composés On n'est pas certain si le feu est pesant. Il y a des expériences pour et contre.

"Pendant la combustion des substances, le feu combiné se réduit en feu élémentaire, et se dissipe à mesure. Le célèbre Boerhaave n'est cependant pas de ce sentiment ; il dit que si cela étoit, la quantité de feu élémentaire devrait augmenter à l'infini dans la nature. Mais il est facile de répondre à cette objection, en disant comme on est en droit de le présumer, que le feu élémentaire, dégagé des corps, se combine à mesure avec d'autres substances, et qu'il perd toutes ses propriétés de feu libre, en devenant principe constituant des corps, dans la composition desquels il entre. Le principe dont nous entendons parler ici, est celui que Stahl a nommé *phlogistique*."

In interpreting the above and other phlogistic writings by the light of modern doctrine, it is not meant to attribute to their several authors the precise notion of energy that now prevails. It is contended only that the phlogistians had, in their time, possession of a real truth in nature which, altogether lost sight of in the intermediate period, has since crystallized out in a definite form. "I trust," said Beccher, "that I have got hold of my pitcher by the right handle." And what he and his followers got hold of and retained so tenaciously, though it may be shiftingly and ignorantly, we now hold to knowingly, definitely, and quantitatively, as part and parcel of the grandest generalization in science that has ever yet been established.

[W. O.]

Friday, May 26, 1871.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

W. J. MACQUORN RANKINE, C.E. LL.D. F.R.S.

On Sea Waves.

THE speaker in the first place gave a summary, illustrated by diagrams and machines, of existing knowledge of the mode of motion of water in waves, and of the geometrical and dynamical laws which govern the relations between the depth of disturbance of the water, the velocity of advance of waves, their periodic time, and their length. He referred to the experimental and theoretical researches of previous authors on the subject, such as the Webers, Airy, Scott Russell, Caligny, &c.

He then explained the principle, of which Mr. Froude was the first to point out the importance, that the action of water agitated by waves upon a ship tends to make her perform the motions which would have been performed in her absence by the mass of water that she displaces. In still water, the forces of gravity and of buoyancy tend to keep the ship upright, and if she has been heeled over, to restore her to the upright position, and that tendency constitutes the *statical stability* or *stiffness* of the ship. Amongst waves the same forces, combined with the reactions due to the heaving motions of the water and of the ship, tend to place her in the position called *upright to the wave surface*; that is, with her originally vertical axis normal to the wave surface. If the ship yielded passively to that tendency, like a broad and shallow raft, she would accompany the waves in their rolling; and thus, a ship having great *stiffness* may be very deficient in *steadiness*. Every ship has, like a pendulum, a natural period of rolling, depending on her stiffness, or tendency to right herself, and her moment of inertia, being a quantity depending on the distribution of her mass. Stiffness tends to shorten, and inertia to lengthen, the period. It was shown in 1862, by Mr. Froude, that the greatest unsteadiness and the greatest danger of being overturned take place when the periodic times of rolling of the ship and of the waves are equal; for then each successive wave adds to the extent of roll; and if the coincidence of the periods were exact, the ship would inevitably be overturned in the end.

In the course of the present spring it has been pointed out that in well-designed ships a safeguard exists against the occurrence of such disasters. It is well known that no pendulum is absolutely isochronous; but great oscillations occupy a longer time than small oscillations. In like manner, no ship is absolutely isochronous in her natural rolling;

but great angles of roll occupy longer periods than small.* Hence, supposing a ship to encounter waves of a period equal or nearly equal to her own natural period for small angles of roll, her angle of rolling is at first progressively increased; but at the same time her natural periodic time of rolling is increased, until it is no longer equal or nearly equal to the periodic time of the waves; and thus she in a manner *eludes* the danger arising from coincidence of periods. In order, however, that this safeguard may act efficiently, it is essential that the natural period of the ship for the smallest angles of roll should not be less than the period of the waves; otherwise the first effect of the progressive increase of angle will be, not to destroy, but to produce coincidence of period; and the result will be great unsteadiness of motion, and possibly great danger.

The speaker described the above principles as being the latest additions to our knowledge of the theory of the relations between ships and sea-waves; and he illustrated them by means of experiments on a machine so constructed as to imitate the dynamical condition of a ship rolling amongst waves.

[W. J. M. R.]

* *Note* (added 2nd June).—An exception to this rule exists in the case of that form of ship known as the “Symondite,” in which the sides flare out at and near the water-line, so as to make the stiffness increase faster than the angle of heel. In such ships the period of rolling *shortens* when the angle increases; and thus the well-known unsteadiness of large vessels of that model is accounted for. In a small boat, whose natural periodic time for the smallest angle of roll is shorter than that of any of the waves which she encounters, the Symondite model does not promote unsteadiness; for the shortening of the natural period of rolling removes it farther from coincidence with the period of the waves.

Friday, June 2, 1871.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

THOMAS ANDREWS, M.D. F.R.S.

VICE-PRESIDENT OF QUEEN'S COLLEGE, BELFAST,

On the Gaseous and Liquid States of Matter.

THE liquid state of matter forms a link between the solid and gaseous states. This link is, however, often suppressed, and the solid passes directly into the gaseous or vaporous form. In the intense cold of an Arctic winter hard ice will gradually change into transparent vapour without previously assuming the form of water. Carbonic acid snow passes rapidly into gas when exposed to the air, and can with difficulty be liquefied in open tubes. Its boiling point, as Faraday has shown, presents the apparent anomaly of being lower in the thermometric scale than its melting point; a statement less paradoxical than it may at first appear, if we remember that water can exist as vapour at temperatures far lower than those at which it can exist as liquid. Whether the transition be directly from solid to gaseous, or from solid to liquid, and from liquid to gaseous, a marked change of physical properties occurs at each step or break, and heat is absorbed, as was proved long ago by Black, without producing elevation of temperature. Many solids and liquids will for this reason maintain a low temperature, even when surrounded by a white hot atmosphere, and the remarkable experiment of solidifying water, and even mercury, on a red-hot plate, finds thus an easy explanation. The term spheroidal state, when applied to water floating on a cushion of vapour over a red-hot plate, is however apt to mislead. The water is not here in any peculiar state. It is simply water evaporating rapidly at a few degrees below its boiling point, and all its properties, even those of capillarity, are the properties of ordinary water at 96.5 C. The interesting phenomena exhibited under these conditions are due to other causes, and not to any new or peculiar state of the liquid itself. The fine researches of Dalton upon vapours, and the memorable discovery by Faraday of the liquefaction of gases by pressure alone, finished the work which Black had begun. Our knowledge of the conditions under which matter passes abruptly from the gaseous to the liquid, and from the liquid to the solid state, may now be regarded as almost complete.

In 1822 Cagniard de La Tour made some remarkable experiments,

which still bear his name, and may be regarded as the starting-point of the investigations which form the chief subject of this address. Cagniard de La Tour's first experiments were made in a small Papin's digester, constructed from the thick end of a gun-barrel, into which he introduced a little alcohol and also a small quartz ball, and firmly closed the whole. On heating the gun-barrel with its contents over an open fire, and observing from time to time the sound produced by the ball when the apparatus was shaken, he inferred that after a certain temperature was attained the liquid had disappeared. He afterwards succeeded in repeating the experiment in glass tubes, and obtained the following results:—An hermetically-sealed glass tube, containing sufficient alcohol to occupy two-fifths of its capacity, was gradually heated, when the liquid was seen to dilate, and its mobility at the same time to become gradually greater. After attaining to nearly twice its original volume, the liquid completely disappeared, and was converted into a vapour so transparent that the tube appeared to be quite empty. On allowing the tube to cool, a very thick cloud was formed, after which the liquid reappeared in its former state.

It is singular that in this otherwise accurate description, Cagniard de La Tour should have overlooked the most remarkable appearance of all, the moving or flickering striæ, which fill the tube when, after heating it considerably, the temperature is quickly lowered. This phenomenon was first described by myself in 1863, as it is seen in carbonic acid, which has been partially liquified by pressure, and afterwards heated a little above 31° . It may be observed on a larger scale and to great advantage by heating such liquids as sulphurous acid or ether in hermetically-sealed tubes.

The experiments whose results I am about to describe have occupied me for a period of fully ten years; they involved the construction of novel forms of apparatus, in which the properties of matter might be studied under varied conditions of temperature and pressure, such as had never been realized before. In my earlier attempts I endeavoured, as others had already done, to use the expansive force of the mixed gases which are disengaged in the electrolysis of water; and I was able in this way to obtain pressures of 150 atmospheres and even more in glass tubes; but the method was in many respects defective, and more than one dangerous explosion occurred, so that I eventually abandoned it.

In the apparatus finally adopted, the gas to be compressed is enclosed in a long glass tube, of which the greater part of the length, or about 450 millimetres, has a capillary bore, and the remainder, about 150 millimetres, an internal diameter of 2 millimetres. The free capillary end is sealed, while the gas in a pure and dry state is passing through; while at the other end the gas is confined by a movable column of mercury. The details of the method by which this is accomplished will be found in the Bakerian lecture for 1869, to which I must also refer for an account of the process by which the original volume of the gas at the freezing point of water and

under one atmosphere of pressure was determined, and also the volumes of the same gas deduced from the observed measurements when it was compressed at different pressures in the capillary tube.

A conical protuberance on the capillary part of the tube, a little above its junction with the wider part, corresponded as nearly as possible with a hollow cone in a stout brass flange, the joint being rendered perfectly tight by careful packing. The body of the apparatus consisted of two cold-drawn copper tubes of great strength, to the ends of which four massive brass flanges were firmly attached. Two corresponding flanges or end pieces, each carrying a fine steel screw packed with great care, were bolted on the lower flanges. The success of the experiments depended greatly on the packing of this screw. It was effected by means of a number of leather washers, tightly pressed down and saturated *in vacuo* with melted lard. The apparatus was now filled with water; the flanges with the glass tubes, one containing the gas to be examined, the other air or hydrogen to act as a manometer or measure of the pressure, were bolted down upon the upper flanges of the copper tubes. The joints had always leather washers interposed; and when sufficiently tightened, they resisted any pressure which could be applied, even for an indefinite time. The two copper tubes were connected by a fine horizontal tube, so that the whole of the interior of the apparatus was in free communication. The pressure was obtained by screwing one or other of the steel screws into the water. I have recently had the apparatus constructed of iron and filled with mercury. As mercury is much less compressible than water, the same length of screw produces a greater pressure on the interior of the apparatus, even with a larger cavity. There are other advantages in this form of the apparatus which I hope will facilitate future research. The objection to it is its extreme sensitiveness to changes of temperature, so that a variation of $\frac{1}{100}$ th of a degree alters the internal pressure by several atmospheres.

In the actual experiments the gas under examination does not come into view till it has entered the capillary tube, and is exposed to a pressure of thirty or forty atmospheres. The limit of the pressure which can be obtained has hitherto been the capacity of resistance of the glass tubes to bursting. Fine thermometer glass tubes of white glass will frequently burst when exposed to a pressure of little more than 100 atmospheres; but green glass tubes of good quality are much stronger, and will easily bear a pressure of 300 atmospheres. One of the strongest forms of glass capillary tube for resisting internal pressure is obtained by drawing out a thick green glass tube, heated to softening, till it becomes so fine as to be flexible. Tubes of this kind can easily be drawn out at the blowpipe table, and obtained of very uniform bore. I have compressed air in such tubes to $\frac{1}{400}$ th of its ordinary volume without bursting the tubes.

Two rectangular brass cases, closed before and behind with plate-glass, surround, one the manometer, and the other the tube containing

the gas to be examined, and allow them to be maintained at any required temperature by the flow of a stream of water. The manometer was maintained as nearly as possible at the temperature of the apartment; the tube containing the gas, on the contrary, was maintained at different temperatures, according to the object in view. The following observations, published in 1863, contain the results of my earliest experiments on this subject:—"On partially liquefying carbonic acid by pressure alone, and gradually raising the temperature at the same time to 88° Fahr., the surface of demarcation between the liquid and gas becomes fainter, loses its curvature, and at last disappears. The space is then occupied by a homogeneous fluid, which exhibits when the pressure is suddenly diminished or the temperature slightly lowered, a peculiar appearance of moving or flickering stræ throughout its entire mass. At temperatures above 88° no apparent liquefaction, or separation into two distinct forms of matter, could be effected, even when a pressure of 300 or 400 atmospheres was applied. Nitrous oxide gave analogous results."

The flickering stræ referred to can be admirably shown, as I mentioned before, in hermetically-sealed tubes of strong glass, partially filled with such liquids as sulphurous acid or ether. The liquid must in the first instance be heated a few degrees above what I have designated the "critical" point. The appearances exhibited by the ascending and descending sheets of matter of unequal density are most remarkable, but must be seen in order to be understood. They only occur in this striking form in fluids heated a little above the critical point, and are produced by the great changes of density which slight variations of pressure or temperature produce in this case. They are always a clear proof that the matter in the tube is homogeneous, and that we have not liquid and gas in presence of one another. These stræ are in short only an extraordinary development of the movements seen in ordinary liquids and gases when they are heated from below. The experiments to be immediately described will explain their great intensity above the critical point.

When the temperature falls below the critical point, the formation of a cloud indicates that we have now heterogeneous matter in the tube, fine drops of liquid in presence of a gas. We must take care, however, not to suppose that a cloud *necessarily* precedes the formation of true liquid. If the pressure be sufficiently great no cloud of any kind will form.

I now proceed to describe the general results of the experiments upon carbonic acid. If a certain volume of carbonic acid at the temperature of 13°·1 and under a pressure of one atmosphere be exposed to a gradually-increasing pressure, its volume will steadily diminish, but at a faster rate than according to Boyle's law, till at the pressure of 48·9 atmospheres its volume is reduced to about $\frac{1}{11}$ of the original volume at one atmosphere. Liquefaction now begins and continues with very slight augmentation of pressure, the necessity for which I traced to the presence of a minute quantity of air (about $\frac{1}{2500}$ th part)

in the carbonic acid. On augmenting the pressure after liquefaction, the volume slowly diminished, but at a much faster rate than in the case of ordinary liquids. Later experiments carried to much higher pressures have fully confirmed this result. At $21^{\circ}\cdot5$ similar results were obtained, but a pressure of nearly 60 atmospheres was required before liquefaction began.

At $30^{\circ}\cdot9$ C., or $87^{\circ}\cdot7$ Fahr., the critical point of temperature is reached. It is the temperature at which liquid ceases to be formed under any pressure. At a temperature a little below this point the surface of separation between liquid and gas becomes very faint and loses its curvature, the density and other physical properties of the liquid and gas being now identical and the tube filled with homogeneous matter. If the temperature and pressure be kept steady, no evidence of heterogeneity will be obtained by optical tests under the most varied conditions of volume.

If we now follow the course of a given volume of carbonic acid gas at $31^{\circ}\cdot1$, or $0^{\circ}\cdot2$ above the critical point, we shall find that its course resembles that of the gas at lower temperatures till the volume is reached at which liquefaction might be expected to begin. A rapid but not (as in the case of the formation of liquid) abrupt fall then supervenes, after which the carbonic acid undergoes a slow diminution of volume as the pressure augments. The curves, which are here exhibited as they were represented in the Bakerian lecture, illustrate very clearly these statements. We have thus carbonic acid at $0^{\circ}\cdot2$ above the critical point, and at a pressure of 73 atmospheres behaving very nearly as if it liquefied. At this pressure an augmentation of only $\frac{1}{3}$ th of the entire pressure diminishes the volume of the carbonic acid to about one half. Yet during the whole of this fall, no evidence of heterogeneity, or of two states of matter present together in the tube, could at any period be obtained. Carbonic acid at this temperature of $31^{\circ}\cdot1$, and under a pressure of 75 atmospheres, behaves much more as a liquid than as a gas when the pressure is either augmented or diminished; yet it never exhibits under any conditions the characteristic properties of the liquid state; that is to say, no surface of separation is formed by change of pressure, nor will it collect into drops and form a cloud.

At $32^{\circ}\cdot5$ the fall, when liquefaction might be expected, is less abrupt than at $31^{\circ}\cdot1$; and at $35^{\circ}\cdot5$, although still manifest, it is further reduced. At $48^{\circ}\cdot1$ the fall shown at lower temperatures can no longer be distinctly observed, and the curve representing the change of volume approximates to that of a perfect gas. There can be little, if any, doubt that at a higher temperature carbonic acid would behave under augmenting pressures nearly as nitrogen or hydrogen.*

* These different modes of passing from the gaseous to the liquid state are admirably illustrated by a solid model constructed by Prof. J. Thomson, which was exhibited at the lecture. I have been favoured by Prof. Thomson with the following description of this model:—

I have frequently exposed carbonic acid, without making precise measurements, to much higher pressures than any of the foregoing, and have made it pass without break or interruption from what is regarded by every one as the gaseous state, to what is, in like manner, universally regarded as the liquid state. Take, for example, a given volume of carbonic acid gas at 50° C., or at a higher temperature, and expose it to increasing pressure till 150 atmospheres have been reached. In this process its volume will steadily diminish as the pressure augments, and no sudden diminution of volume, without the application of external pressure will occur at any stage of it. When the full pressure has been applied, let the temperature be allowed to fall till the carbonic acid has reached the ordinary temperature of the atmosphere. During the whole of this operation no breach of continuity has occurred. It begins with a gas, and by a series of gradual changes, presenting nowhere any abrupt alteration of volume or sudden evolution of heat, it ends with a liquid. The closest observation fails to discover anywhere indications of a change of condition in the carbonic acid, or evidence, at any period of the process, of part of it being in one physical state and part in another. That the gas has actually changed into a liquid would, indeed, never have been suspected, had it not shown itself to be so changed by

"The model combines Dr. Andrews' experimental results in a manner tending to show clearly their mutual correlation. It consists of a curved surface referred to three axes of rectangular co-ordinates, and formed so that the three co-ordinates of each point in the curved surface represent, for any given mass of carbonic acid, a pressure, a temperature, and a volume, which can co-exist in that mass.

"In Dr. Andrews' diagram of curves, published in his paper in the 'Transactions of the Royal Society for 1869,' p. 583, the experimental results, for each of several temperatures experimented on, are combined in the form of a plane curved line referred to two axes of rectangular co-ordinates. The curved surface in the model is obtained by placing these curved lines with their planes parallel to one another, and separated by intervals proportional to the differences of the temperatures to which the curves severally belong, and with the origins of co-ordinates of the curves situated in a straight line perpendicular to their planes, and with the axes of co-ordinates of all of them parallel in pairs to one another, and by cutting the curved surface out so as to pass through those curved lines smoothly or evenly.

"The curved surface so obtained exhibits in a very obvious way the remarkable phenomena of the voluminal conditions at and near the critical point of temperature and pressure in comparison with the voluminal conditions throughout other parts of the indefinite range of gradually varying temperatures and pressures. This curved surface also helps to afford a clear view of the nature and meaning of the continuity of the liquid and gaseous states of matter. It does so by its own obvious continuity throughout the expanse to which it might be extended round the outside of the critical point in receding from the range of the points of pressure and temperature where an abrupt change of volume can occur by gasification or condensation. On the curved surface in the model, Dr. Andrews' curves for the temperatures 13° ·1, 21° ·5, 31° ·1, 35° ·5, and 48° ·1 centigrade, from which it was constructed, are shown drawn in their proper places. The model admits of easily exhibiting in due relation to one another a second set of curves in which each curve would be for a constant pressure, and in which the co-ordinates would represent temperatures and corresponding volumes. It serves generally as an aid towards bringing the whole subject clearly before the mind."

entering into ebullition on the removal of the pressure. For convenience, this process has been divided into two stages, the compression of the carbonic acid and its subsequent cooling; but these operations might have been performed simultaneously, if care were taken so to arrange the application of the pressure and the rate of cooling, that the pressure should not be less than 76 atmospheres when the carbonic acid had cooled to 31° .

We are now prepared for the consideration of the following important question. What is the condition of carbonic acid when it passes, at temperatures above 31° , from the gaseous state down to the volume of the liquid, without giving evidence at any part of the process of liquefaction having occurred? Does it continue in the gaseous state, or does it liquefy, or have we to deal with a new condition of matter? If the experiment were made at 100° , or at a higher temperature, when all indications of a fall had disappeared, the probable answer which would be given to this question is that the gas preserves its gaseous condition during the compression; and few would hesitate to declare this statement to be true, if the pressure were applied to such gases as hydrogen or nitrogen. On the other hand, when the experiment is made with carbonic acid at temperatures a little above 31° , the great fall which occurs at one period of the process would lead to the conjecture that liquefaction had actually taken place, although optical tests carefully applied failed at any time to discover the presence of a liquid in contact with a gas. But against this view it may be urged with great force, that the fact of additional pressure being always required for a further diminution of volume, is opposed to the known laws which hold in the change of bodies from the gaseous to the liquid state. Besides, the higher the temperature at which the gas is compressed, the less the fall becomes, and at last it disappears. .

The answer to the foregoing question, according to what appears to me to be the true interpretation of the experiments already described, is to be found in the close and intimate relations which subsist between the gaseous and liquid states of matter. The ordinary gaseous and ordinary liquid states are, in short, only widely separated forms of the same condition of matter, and may be made to pass into one another by a series of gradations so gentle that the passage shall nowhere present any interruption or breach of continuity. From carbonic acid as a perfect gas to carbonic acid as a perfect liquid, the transition we have seen may be accomplished by a continuous process, and the gas and liquid are only distant stages of a long series of continuous physical changes. Under certain conditions of temperature and pressure, carbonic acid finds itself, it is true, in what may be described as a state of instability, and suddenly passes, with evolution of heat, and without application of additional pressure or change of temperature, to the volume, which by the continuous process can only be reached through a long and circuitous route. In the abrupt change which here occurs, a marked difference is exhibited,

while the process is going on, in the optical and other physical properties of the carbonic acid which has collapsed into the smaller volume, and of the carbonic acid not yet altered. There is no difficulty here, therefore, in distinguishing between the liquid and the gas. But in other cases the distinction cannot be made; and under many of the conditions I have described it would be vain to attempt to assign carbonic acid to the liquid rather than the gaseous state. Carbonic acid, at the temperature of $35^{\circ}5$, and under a pressure of 108 atmospheres, is reduced to $\frac{1}{410}$ of the volume it occupied under a pressure of one atmosphere; but if anyone ask whether it is now in the gaseous or liquid state, the question does not, I believe, admit of a positive reply. Carbonic acid at $35^{\circ}5$, and under 108 atmospheres of pressure, stands nearly midway between the gas and the liquid; and we have no valid grounds for assigning it to the one form of matter any more than to the other. The same observation would apply with even greater force to the state in which carbonic acid exists at higher temperatures and under greater pressures than those just mentioned. In short, the passage under great pressures from the liquid to the gaseous state may be effected by the application of heat without break or breach of continuity. That a marked change in the physical properties of the substance occurs during this process is no objection to its being continuous. If mercury as a liquid is opaque and as a gas is transparent, the red and translucent bromine, on the other hand, when heated above the critical point, becomes so opaque as almost to resemble a mass of resin. Frankland has shown that the flame of hydrogen becomes continuous when the gas is burned under a pressure of 20 atmospheres, and these experiments have been since extended by the same able chemist and Lockyer. We must not, however, suppose that one intermediate state exists between liquid and gas; on the contrary, an infinite succession of intermediate states may truly be said to connect the liquid proper and the gas proper; in other words, the passage is continuous. When the critical point is attained, the density of the liquid and gas becomes the same, and the tube is filled with homogeneous matter.

As regards the question of the continuity of the solid and liquid states, it would be necessary, in order to establish this continuity, to obtain, by the combined action of heat and pressure, the solid and liquid of the same density and of like physical properties. To accomplish this result will probably require pressures far beyond any which can be reached in transparent tubes; but it may be possible to show by experiment that the solid and liquid can be made to approach to the required conditions.

[T. A.]

Friday, June 9, 1871.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

JOHN TYNDALL, Esq. LL.D. F.R.S.

PROFESSOR OF NATURAL PHILOSOPHY, ROYAL INSTITUTION,

On Dust and Smoke.

AFTER a few preliminary experiments illustrative of the polarization of light, Professor Tyndall adverted to the polarization of light by fine dust, by the sky, and by the coarser particles of smoke. In the former the direction of maximum polarization, as in the case of the sky, is at right angles to the illuminating beam. In the latter, according to the observations of Govi, the maximum quantity of polarized light was discharged obliquely to the beam. Govi's observation of a neutral point in such beam, on one side of which the polarization was positive and on the other side negative, was also referred to. The additional fact was then adduced that the position of the neutral point varied with the density of the smoke. Beginning, for example, with an atmosphere thickened by the dense fumes of incense, resin, or gunpowder, and observing the neutral point, its direction was first observed to be inclined to the beam *towards* the source of illumination. Opening the windows so as to allow the smoke to escape gradually, the neutral point moved down the beam, passed the end of a normal drawn to the beam from the eye, and gradually moved forward several feet down the beam. The speaker did not halt at these observations; they were introduced as the starting-point of inquiries of a different nature, and after their introduction the discourse proceeded thus:—

But what, you may ask, is the practical good of these curiosities? And if you so ask, my object is in some senses gained, for I intended to provoke this question. I confess that if we exclude the interest attached to the observation of new facts, and the enhancement of that interest through the knowledge that by-and-by the facts will become the exponents of laws, these curiosities are in themselves worth nothing. They will not enable us to add to our stock of food, or drink, or clothes, or jewellery. But though thus shorn of all usefulness in themselves, they may, by leading the mind into places which it would not otherwise have entered, become the antecedents of practical consequences. In looking, for example, at this illuminated dust, we may ask ourselves what it is. How does it act, not upon a beam of light, but upon our own lungs and stomachs? The question at once assumes a practical character. We find on examination that this dust is organic matter—in part living, in part dead. There are among it particles of ground straw, torn rags, smoke, the pollen of flowers, the

spores of fungi, and the germs of other things. But what have they to do with the animal economy? Let me give you an illustration to which my attention has been lately drawn by Mr. George Henry Lewes, who writes to me thus:—

“I wish to direct your attention to the experiments of Von Recklingshausen should you happen not to know them. They are striking confirmations of what you say of dust and disease. Last spring, when I was at his laboratory in Wurzburg, I examined with him blood that had been three weeks, a month, and five weeks, out of the body, preserved in little porcelain cups under glass shades. This blood was living and growing. Not only were the Amœba-like movements of the white corpuscles present, but there were abundant evidences of the growth and development of the corpuscles. I also saw a frog’s heart still pulsating which had been removed from the body (I forgot how many days, but certainly more than a week). There were other examples of the same persistent vitality or absence of putrefaction. Von Recklingshausen did not attribute this to the absence of germs—germs were not mentioned by him; but when I asked him how he represented the thing to himself, he said the whole mystery of his operation consisted in keeping the blood *free from dirt*. The instruments employed were raised to a red heat just before use, the thread was silver thread and was similarly treated, and the porcelain cups, though not kept free from air, were kept free from currents. He said he often had failures, and these he attributed to particles of dust having escaped his precautions.”

Professor Lister, who has founded upon the removal or destruction of this “dirt” great and numerous improvements in surgery, tells us the effect of its introduction into the blood of wounds. He informs us what would happen with the extracted blood should the dust get at it. The blood would putrefy and become fetid; and when you examine more closely what putrefaction means, you find the putrefying substance swarming with organic life, the germs of which have been derived from the air.

Another note which I received a day or two ago has a bearing particularly significant at the present time upon this question of dust and dirt, and the wisdom of avoiding them. The note is from Mr. Ellis, of Sloane Street, to whom I owe a debt of gratitude for advice given to me when sorely wounded in the Alps. “I do not know,” writes Mr. Ellis, “whether you happened to see the letters, of which I enclose you a reprint, when they appeared in ‘The Times.’ But I want to tell you this in reference to my method of vaccination as here described; because it has, as I think, a relation to the subject of the intake of organic particles from without into the body. Vaccination in the common way is done by scraping off the epidermis, and thrusting into the punctures made by the lancet the vaccine virus. By the method I use (and have used for more than twenty years) the epidermis is lifted by the effusion of serum from below, a result of the irritant cantharidine applied to the skin. The little bleb thus formed

is pricked, a drop of fluid let out, and then a fine vaccine point is put into this spot, and after a minute of delay it is withdrawn. The epidermis falls back on the skin, and quite excludes the air—and not the air only, but what the air contains.

“Now mark the result—out of hundreds of cases of re-vaccination which I have performed, I have never had a single case of blood-poisoning or of abscess. By the ordinary way the occurrence of secondary abscess is by no means uncommon, and that of pyæmia is occasionally observed. I attribute the comparative safety of my method entirely, first, to the exclusion of the air and what it contains; and, secondly, to the greater size of the apertures for the inlet of mischief made by the lancet.”

I bring these facts forward that they may be sifted and challenged if they be not correct. If they are correct it is needless to dwell upon their importance, nor is it necessary to say that if Mr. Ellis had resigned himself wholly to the guidance of the germ theory he could not have acted more in accordance with the requirements of that theory than he has actually done. It is what the air contains that does the mischief in vaccination. Mr. Ellis's results fall in with the general theory of putrefaction propounded by Schwann, and developed in this country with such striking success by Professor Lister. They point, if true, to a cause distinct from bad lymph for the failures and occasional mischief incidental to vaccination; and if followed up they may be the means of leaving the irrational opposition to vaccination no ground to stand upon, by removing even the isolated cases of injury on which the opponents of the practice rely.

We are now assuredly in the midst of practical matters. With your permission I will recur once more to a question which has recently occupied a good deal of public attention. You know that as regards the lowest forms of life, the world is divided, and has for a long time been divided, into two parties, the one affirming that you have only to submit absolutely dead matter to certain physical conditions to evolve from it living things; the other, without wishing to set bounds to the power of matter, affirming that in our day no life has ever been found to arise independently of pre-existing life. Many of you are aware that I belong to the party which claims life as a derivative of life. The question has two factors: the evidence, and the mind that judges of the evidence; and you will not forget that it may be purely a mental set or bias on my part that causes me throughout this discussion from beginning to end, to see on the one side dubious facts and defective logic, and on the other side firm reasoning and a knowledge of what rigid experimental inquiry demands. But judged of practically, what, again, has the question of Spontaneous Generation to do with us? Let us see. There are numerous diseases of men and animals that are demonstrably the products of parasitic life, and such diseases may take the most terrible epidemic forms, as in the case of the silkworms of France in our day. Now it is in the highest degree important to know whether the parasites in question are spontaneously

developed, or are wafted from without to those afflicted with the disease. The means of prevention, if not of cure, would be widely different in the two cases.

But this is by no means all. Besides these universally admitted cases, there is the broad theory now broached and daily growing in strength and clearness—daily, indeed, gaining more and more of assent from the most successful workers and profound thinkers of the medical profession itself—the theory, namely, that contagious disease generally is of this parasitic character. If I had heard or read anything since to cause me to regret having introduced this theory to your notice more than a year ago, I should here frankly express that regret. I would renounce in your presence whatever leaning towards the germ theory my words might then have betrayed. Let me state in two sentences the grounds on which the supporters of the theory rely. From their respective viruses you may plant typhoid fever, scarlatina, or small-pox. What is the crop that arises from this husbandry? As surely as a thistle rises from a thistle seed, as surely as the fig comes from the fig, the grape from the grape, the thorn from the thorn, so surely does the typhoid virus increase and multiply into typhoid fever, the scarlatina virus into scarlatina, the small-pox virus into small-pox. What is the conclusion that suggests itself here? It is this:—That the thing which we vaguely call a virus is to all intents and purposes a *seed*: that, excluding the notion of vitality, in the whole range of chemical science you cannot point to an action which illustrates this perfect parallelism with the phenomena of life—this demonstrated power of self-multiplication and reproduction. The germ theory alone accounts for the phenomena.

And here you see the bearing of the doctrine of Spontaneous Generation upon this question. For if the doctrine continues to be discredited as it has hitherto been, it will follow that the epidemics which spread havoc amongst us from time to time are not spontaneously generated, but that they arise from an ancestral stock whose habitat is the human body itself. It is not on bad air or foul drains that the attention of the physician will primarily be fixed, but upon disease germs which no bad air or foul drains can create, but which may be pushed by foul air into virulent energy of reproduction. You may think I am treading on dangerous ground, that I am putting forth views that may interfere with salutary practice. No such thing. If you wish to learn the impotence of medical science and practice in dealing with contagious diseases, you have only to refer to a recent Harveian oration by Dr. Gull. Such diseases defy the physician. They must burn themselves out. And indeed this, though I do not specially insist upon it, would favour the idea of their vital origin. For if the seeds of contagious disease be themselves living things, it will be difficult to destroy either them or their progeny without involving their living habitat in the same destruction.

And I would also ask you to be cautious in accepting the statement which has been so often made, and which is sure to be repeated,

that I am quitting my own *métier* when I speak of these things. I am not dealing with professional questions. I am writing no prescription, nor should I venture to draw any conclusion from the condition of your pulse and tongue. I am dealing with a question on which minds accustomed to weigh the value of experimental evidence are alone competent to decide, and regarding which, in its present condition, minds so trained are as capable of forming an opinion as on the phenomena of magnetism and radiant heat. I cannot better conclude this portion of my story than by reading to you an extract from a letter addressed to me some time ago by Dr. William Budd, of Clifton, to whose insight and energy the town of Bristol owes so much in the way of sanitary improvement.

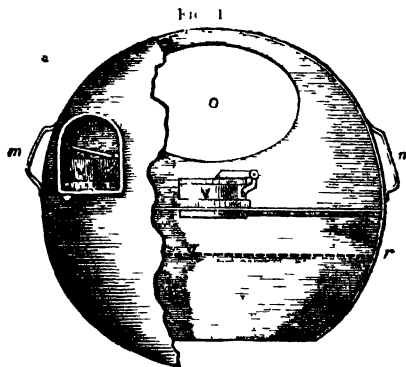
"As to the germ theory itself," writes Dr. Budd, "that is a matter on which I have long since made up my mind. From the day when I first began to think of these subjects, I have never had a doubt that the specific cause of contagious fevers must be living organisms.

"It is impossible, in fact, to make any statement bearing upon the essence or distinctive characters of these fevers, without using terms which are of all others *the most distinctive of life*. Take up the writings of the most violent opponent of the germ theory, and, ten to one, you will find them full of such terms as 'propagation,' 'self-propagation,' 'reproduction,' 'self-multiplication,' and so on. Try as he may—if he has anything to say of those diseases which is characteristic of them—he cannot evade the use of these terms, or the exact equivalents to them. While perfectly applicable to living things, these terms express qualities which are not only inapplicable to common chemical agents, but as far as I can see actually inconceivable of them."

Once then established within the body, this evil form of life, if you will allow me to call it so, must run its course. Medicine as yet is powerless to arrest its progress, and the great point to be aimed at is to prevent its access to the body. It was with this thought in my mind that I ventured to recommend, more than a year ago, the use of cotton-wool respirators in infectious places. I would here repeat my belief in their efficacy if properly constructed. But I do not wish to prejudice the use of these respirators in the minds of its opponents by connecting them indissolubly with the germ theory. There are too many trades in England where life is shortened and rendered miserable by the introduction of matters into the lungs which might be kept out of them. Dr. Greenhow has shown the stony grit deposited in the lungs of stonecutters. The black lungs of colliers is another case in point. In fact, a hundred obvious cases might be cited, and others that are not obvious might be added to them. We should not, for example, think that printing implied labours where the use of cotton-wool respirators might come into play; but I am told that the dust arising from the sorting of the type is very destructive of health. I went some time ago into a manu-

factory in one of our large towns, where iron vessels are enamelled by coating them with a mineral powder, and subjecting them to a heat sufficient to fuse the powder. The organization of the establishment was excellent, and one thing only was needed to make it faultless. In a large room a number of women were engaged covering the vessels. The air was laden with the fine dust, and their faces appeared as white and bloodless as the powder with which they worked. By the use of cotton-wool respirators these women might be caused to breathe air more free from suspended matters than that of the open street. Over a year ago I was written to by a Lancashire seedsman, who stated that during the seed season of each year his men suffered horribly from irritation and fever, so that many of them left his service. He asked me could I help him, and I gave him my advice. At the conclusion of the season this year he wrote to me that he had simply folded a little cotton-wool in muslin, and tied it in front of the mouth; that he had passed through the season in comfort and without a single complaint from one of his men.

The substance has also been turned to other uses. An invalid tells me that at night he places a little of the wool before his mouth, slightly moistening it to make it adhere; that he has thereby prolonged his sleep, abated the irritation of his throat, and greatly mitigated a hacking cough from which he had long suffered. In fact, there is no doubt that this substance is capable of manifold useful applications. An objection was urged against the use of it: that it became wet and heated by the breath. While I was casting about for a remedy for this, a friend forwarded to me from Newcastle a form of respirator invented by Mr. Carrick, an hotel-keeper at Glasgow, which meets the case effectually, and by a slight modification may be caused to meet it perfectly. The respirator, with its back in part removed, is shown in Fig. 1. It consists of the space under the partition of wire gauze *q r*, intended by Mr. Carrick for "medicated substances," and which may be filled with cotton-wool. The mouth is placed against the aperture *O*, which fits closely round the lips, and the air enters the mouth through the cotton-wool by a light valve *V*, which is lifted by the act of inhalation. During exhalation this valve closes; another breath escapes by a second valve, *V'*, into the open air. The wool is thus kept dry and cool; the air in passing through it being filtered of everything it holds in suspension.*



* Mr. Ladd, of Beak Street, sells these respirators.

We have thus been led by our first unpractical experiments into a thicket of practical considerations. In taking the next step, a personal peculiarity had some influence upon me. The only kind of fighting in which I take the least delight, is the conflict of man with nature. I like to see a man conquer a peak or quench a conflagration. I remember clearly the interest I took twenty years ago in seeing the firemen of Berlin contending for mastery with a fire which had burst somewhere near the Brandenburger Thor; and I have often experienced the same interest in the streets of London. Admiring as I do the energy and bravery of our firemen, and having heard that smoke was a greater enemy to them than flame itself, the desire arose of devising a fireman's respirator. But before I describe what has been done in this direction, let me draw your attention to the means hitherto employed to enable a man to live in dense smoke. Thanks to the courtesy of Capt. Shaw, I am enabled to show you the action of the "smoke-jacket," known abroad as the "Appareil Paulin," from its supposed inventor. The jacket is of pliable cowhide. It has arms and a hood, with eye-glasses. With straps and buckles the jacket is tied round the wrists and waist, and a strap which passes between the legs prevents it from rising. On the left side of the jacket is fixed a screw, to which the ordinary hose of the fire-engine is attached, and through the hose air instead of water is urged into the space between the fireman's body and the jacket. It becomes partially inflated, but no pressure of any amount is attainable, because the air, though somewhat retarded, escapes with tolerable freedom from the wrists and waist. Hence the fireman, when his hose is long enough, can deliberately walk into the densest smoke or foulest air. But you see the use of the smoke-jacket necessitates the presence of several men; it also implies the presence of an engine. A single man could make no use of it, nor indeed any number of men without a pumping engine. Its uses are thus summed up in a communication addressed to me by Captain Shaw:—

"This smoke-jacket is very useful for extinguishing fires in vaults, stopping conflagrations in the holds of ships, and penetrating wells, quarries, mines, cesspools, &c.—any places, in short, where the air has become unfit for respiration.

"The special advantages of this jacket are its great simplicity, its facility for use, and the rapidity with which it can be carried about and put on; but its drawback is that it requires the use of an engine or air-pump, and consequently is of no service to one man alone. For this latter reason smoke-jackets, although very effective for enabling us to get into convenient places for extinguishing fires, have very rarely proved of any avail for *saving life*."

Now, it is that very want that I thought ought to be supplied by a suitable respirator. Our fire-escapes are each in charge of a single man, and I wished to be able to place it in the power of each of those men to penetrate through the densest smoke into the recesses of a house, and there to rescue those who would otherwise be suffocated or

burnt. I thought that cotton-wool, which so effectually arrested dust, might also be influential in arresting smoke. It was tried; but, though found soothing in certain gentle kinds of smoke, it was no match for the pungent fumes of a resinous fire, which we employ in our experiments in the laboratory, and which, I am gratified to learn from Captain Shaw, evolves the most abominable smoke with which he is acquainted. I cast about for an improvement, and in conversing on the subject with my friend Dr. Debus, he suggested the use of glycerine to moisten the wool, and render it more adhesive. In fact, this very substance had been employed by the most distinguished advocate of the doctrine of spontaneous generation, M. Pouchet, for the purpose of catching the atmospheric germs. He spread a film of glycerine on a plate of glass, urged air against the film, and examined the dust which stuck to it. The moistening of the cotton-wool with this substance was a decided improvement; still the respirator only enabled us to remain in dense smoke for three or four minutes, after which the irritation became unendurable.* Reflection suggested that in combustion so imperfect as the production of dense smoke implies, there must be numerous hydrocarbons produced, which, being in a state of vapour, would be very imperfectly arrested by the cotton-wool. These in all probability were the cause of the residual irritation; and if these could be removed, a practically perfect respirator might possibly be obtained.

I state the reasoning exactly as it occurred to my mind. Its result will be anticipated by many present. All bodies possess the power of condensing in a greater or less degree gases and vapours upon their surfaces, and when the condensing body is very porous, or in a fine state of division, the force of condensation may produce very remarkable effects. Thus, a clean piece of platinum-foil placed in a mixture of oxygen and hydrogen so squeezes the gases together as to cause them to combine; and if the experiment be made with care, the heat of combination may raise the platinum to bright redness, so as to cause the remainder of the mixture to explode. The promptness of this action is greatly augmented by reducing the platinum to a state of fine division. A pellet of "spongy platinum," for instance, plunged into a mixture of oxygen and hydrogen, causes the gases to explode instantly. In virtue of its extreme porosity, a similar power is possessed by charcoal. It is not strong enough to cause the oxygen and hydrogen to combine like the spongy platinum, but it so squeezes the more condensable vapours, and also acts with such condensing power upon the oxygen of the air, as to bring both within the combining distance, thus enabling the oxygen to attack and destroy the vapours in the pores of the charcoal. In this way, effluvia of all kinds may be virtually burnt up; and this is the principle of the excellent charcoal respirators invented by Dr. Stenhouse. Armed with one of these, you may

* The nose, with its hairs and mucus, acts, though imperfectly, the part of the moistened cotton wool respirator.

go into the foulest-smelling places without having your nose offended. Some of you will remember Dr. Stenhouse lecturing in this room with a suspicious-looking vessel in front of the table. That vessel contained a decomposing cat. It was covered with a layer of charcoal, and nobody knew until told of it what the vessel contained.*

I may be permitted in passing to give my testimony as to the efficacy of these charcoal respirators in providing warm air for the lungs. Not only is the sensible heat of the breath in part absorbed by the charcoal, but the considerable amount of latent heat which accompanies the aqueous vapour from the lungs is rendered free by the condensation of the vapour in the pores of the charcoal. Each particle of charcoal is thus converted into an incipient ember, and warms the air as it passes inwards. This is in entire accordance with the thermometric observations of Dr. Marcet.

But while powerful to arrest vapours, the charcoal respirator is ineffectual as regards smoke. The particles get freely through the respirator. In a series of them tested downstairs, from half a minute to a minute was the limit of endurance. This might be exceeded by Faraday's method of emptying the lungs completely, and then filling them before going into a smoky atmosphere. In fact, each solid smoke particle is itself a bit of charcoal, and carries on it, and in it, its little load of irritating vapour. It is this, far more than the particles of carbon themselves, that produces the irritation. Hence two causes of offence are to be removed: the carbon particles which convey the irritant by adhesion and condensation, and the free vapour which accompanies the particles. The moistened cotton-wool I knew would arrest the first, fragments of charcoal I hoped would stop the second. In the first fireman's respirator, Mr. Carrick's arrangement of two valves, the one for inhalation, the other for exhalation, are preserved. But the portion of it which holds the filtering and absorbent substances is prolonged to a depth of four or five inches (see Fig. 2). On the partition of wire gauze *qr* at the bottom of the space which fronts the mouth is placed a layer of cotton-wool, *C*, moistened with glycerine; then a thin layer of dry wool, *C'*; then a layer of charcoal fragments; a second thin layer of dry cotton-wool, succeeded by a layer of fragments of caustic lime. The succession of the layers may be changed without prejudice to the action. A wire-gauze cover, shown in plan below Fig. 2, keeps the substances from falling out of the respirator. In the densest smoke that we have hitherto employed, the layer of lime has not been found necessary, nor is it shown in the figure; in a flaming building, indeed, the mixture of air with the smoke never permits the carbonic acid to become so dense as to be irrespirable; but in a place where the gas is present in undue quantity, the fragments of lime would materially mitigate its action.

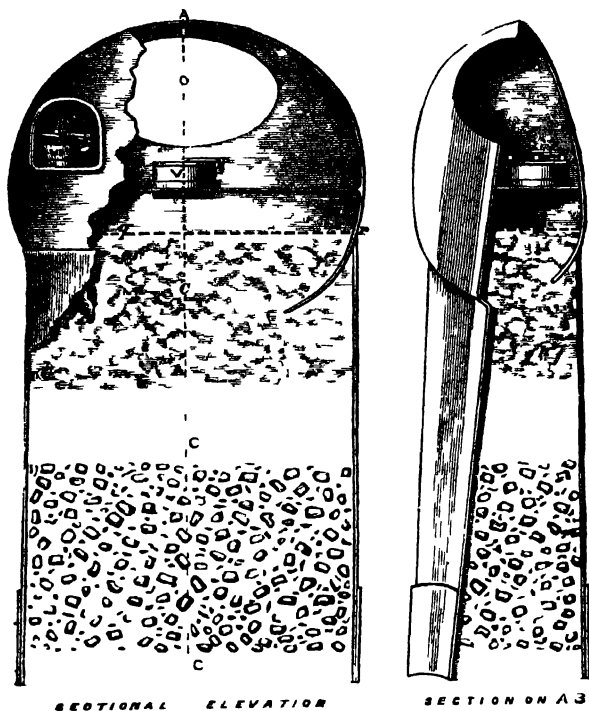
* Dr. Stenhouse has recently shown me a respirator, invented by him many years ago, in which, by means of a single valve, the inhaled air passes through charcoal to the lungs, while that exhaled escapes, without passing through the charcoal, into the open air.

In a small cellar-like chamber downstairs, with a stone flooring and stone walls, the first experiments were made. We placed there furnaces containing resinous pine-wood, lighted the wood, and placing over it a lid which prevented too brisk a circulation of the air, generated dense volumes of smoke. With our eyes protected by suitable glasses, my assistant and I have remained in this room for half an hour and more, when the smoke was so dense and pungent that a single inhalation through the undefended mouth would be perfectly unendurable: and we might have prolonged our stay for hours. Having thus far perfected the instrument, I wrote to Captain Shaw, the chief officer of the Metropolitan Fire Brigade, asking him whether such a respirator would be of use to him. His reply was prompt; it would be most valuable. He had, however, made himself acquainted with every contrivance of the kind in this and other countries, and had found none of them of any practical use. He offered to come and test it here, or to place a room at my disposal in the City. At my request he came here, accompanied by three of his men. Our small room was filled with smoke to their entire satisfaction. The three men went successively into it, and remained there as long as Captain Shaw wished them. On coming out they said that they had not suffered the slightest inconvenience; that they could have remained all day in the smoke. Captain Shaw then tested the instrument with the same result. From that hour the greatest interest has been taken in the perfecting of the instrument by Captain Shaw himself. He has attached to the respirator suitable hoods. The real problem is practically solved, and I can only say that if a tithe of the zeal, intelligence, and practical skill were bestowed on the cotton-wool respirator that Captain Shaw has devoted to the fireman's respirator the sufferings of many a precious life might be spared and its length augmented.*

The discourse was concluded as follows:—"Thus have we been led from the actinic decomposition of vapours through the tails of comets and the blue of the sky to the dust of London, from the germ theory of disease down to this fireman's respirator. Instead of this trivial example, I could, if time permitted, point to others of a more considerable kind in illustration of the tendency of pure science to lead to practical applications. Indeed those very wanderings of the scientific intellect which at first sight appear utterly unpractical, become in the end the wellsprings of practice. Yet I believe there is a philosophy embraced by some of our more ardent thinkers (who I fear on many points commit the well-intentioned, but fatal mistake of putting their own hopeful fancies in the place of fact) that would abolish these wanderings of the intellect and fix it from the outset on practical ends alone. I do not think that that philosophy will ever make itself good in the world, or that any freedom-loving student of nature could or would tolerate its chains."

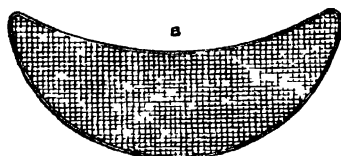
* Mr. Ladd has also proposed a form of mouth-piece which promises well, and Mr. Cottrell has attached to it an ordinary fencing-mask. This will probably be the form of apparatus finally adopted.

FIG. 2



SECTIONAL ELEVATION

SECTION ON A3



PLAN OF BOTTOM COVER

A short time before the discourse I had an opportunity of inspecting the apparatus of Mr. Sinclair, which has been tested and highly spoken of by the superintendent of the Manchester Fire Brigade. The original idea is due to Von Humboldt, who proposed it for the Hartz mines. Galibert constructed the apparatus in an improved form, and it has been still further improved by Mr. Sinclair, who has purchased Galibert's patent. It consists of an air-tight bag, from which issue two tubes that unite on a single one with a respirator mouth-piece. The bag is filled with air, and the wearer inspires through one valve and expires through another. The expired breath is carried to the bottom of the bag, and is stated to remain there in consequence of the chilling experienced in its passage downwards. A bag of not inordinate size is said to be sufficient to supply a man with air for twenty minutes. Mr. Sinclair's apparatus was exhibited during the discourse.

[J. T.]

Friday, January 19, 1872.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM ODLING, Esq. M.B. F.R.S.

FULLERIAN PROFESSOR OF CHEMISTRY, R.I.

On the last new Metal, Indium.

THE word "element" is used by chemists in a peculiar and very limited sense. In calling certain bodies elements, there is no intention on the part of chemists to assert the undecomposable nature or essence of the bodies so called. There is not even an intention on their part to assert that these bodies may not suffer decomposition in certain of the processes to which they are occasionally subjected; but only to assert that they have not hitherto been proved to suffer decomposition; or, in other words, to assert that their observed behaviour under all the different modes of treatment to which they have been exposed, is consistent with the hypothesis of their not having undergone decomposition.

The entire matter of the earth then, so far as chemists are yet acquainted with it, is composed of some sixty-three different sorts of matter that are spoken of as elementary; not because they are conceived to be in their essence primitive or elementary, but because, neither in the course of nature nor in the processes of art, have they been observed to suffer decomposition. No one of them has ever been observed to suffer the loss of any substance different from the substance of its entirety, so as to leave a residuary substance different from the substance of its entirety. Thus chemists are incapable of taking away from iron, for example, a something that is not iron; or of taking away from it anything whatever, so as to leave a residue that is not iron; whereas they are capable of taking away from iron-pyrites a something which is not iron-pyrites but is sulphur, so as to leave a residue which is not iron-pyrites but is metallic iron.

The notion of all other material bodies being constituted of, and decomposable into a limited number of elementary bodies, which could not themselves be proved to suffer decomposition or mutual transformation under any circumstances whatever, but could, on the contrary, be traced respectively through entire series of combinations, and be extracted at will from each member of the series, is a notion which, undergoing in course of time a gradual development, was first

put forward in a definite form by Lavoisier ; until whose time, some residue of the great alchemical doctrine of the essential transmutability of all things—that the substance of all things was the same, while the form above was different—still prevailed. To Lavoisier is due the enunciation of the principle—departed from, however, in a few instances by himself,—that all bodies which cannot be proved to be compounded, are in practical effect, if not in absolute fact, elementary, and are to be dealt with accordingly.

Of the many definite substances known to chemists before the discovery of hydrogen gas, the following were afterwards recognized by Lavoisier and his colleagues as elementary. First, the seven metals known to the ancients, namely, gold, silver, mercury, copper, iron, tin, and lead, distinguished respectively by the signs of the sun, moon, and planets ; and each conceived to have some mystic connection with the particular orb or planet of which it bore the sign, and not unfrequently the name. Then three metals which became known at the latter end of the fifteenth or beginning of the sixteenth century, namely, antimony, discovered by Basil Valentine in 1490 ; bismuth, mentioned by Agricola, 1530 ; and zinc, mentioned by Paracelsus, ob. 1541. An elementary character was also assigned to the non-metals carbon and sulphur, which had been known from the earliest times ; to phosphorus, discovered by Brandt, of Hamburg, in 1669 ; and to boracic acid, now known to be a hydrated oxide of boron, first discovered by Homberg in 1702, and still occasionally spoken of as Homberg's sedative salt. The list was further swelled by four metals which, in Lavoisier's time, had been but recently discovered, namely, cobalt and arsenic, identified simultaneously in 1733 by George Brandt, of Stockholm ; platinum, discovered in 1741 by Woods, assay-master at Jamaica ; and nickel, discovered in 1751 by Cronstedt.

The only other bodies known before 1766, and afterwards included in the class of elements, namely, the alkalies and earths, had during the quarter of a century immediately preceding been made the subjects of especial study. The differentiation of potash from soda, both previously known by the common name of alkali, was indicated by Duhamel in 1736, and more completely established by Marggraf in 1758. The differentiation from one another of lime or calcareous earth, silex or vitreifiable earth, alumina or argillaceous earth, and magnesia or bitter earth, was accomplished by the labour of many chemists, more particularly Marggraf, Bergmann, and Scheele ; prior to whose researches silex, alumina, and magnesia, together with their different combinations and commixtures with each other and with lime, were held to be but impure varieties of lime. The nature of the difference between the caustic alkalies and earths and their respective carbonates, was made known by Black in 1756 ; while the real constitution of the alkalies and earths, as metallic oxides, though suspected by Lavoisier, was not established until the beginning of the present century, by Davy and his contemporaries and followers.

TABLE I.—ELEMENTS, &c., IN ORDER OF DISCOVERY.

..	GOLD	☉	1774	MANGANESE ..	Gahn.
..	SILVER	☽	"	BARYA-IUM ..	Scheele.
..	MERCURY ..	☿	1778	MOLYBDENUM ..	Delhuart.
..	COPPER	♄	1781	TUNGSTEN ..	
..	IRON	♂	1782	TELLURIUM ..	Muller.
..	TIN	♁	1789	URANIUM ..	Klaproth.
..	LEAD	♄	"	ZIRCONIA-IUM ..	
1490	ANTIMONY ..	B. Valentine.	1791	TITANIUM ..	Gregor.
1530	BISMUTH ..	Agricola?	1793	STRONTIA-IUM ..	Hope.
1511	ZINC	Paracelsus?	1794	YTTRIA-IUM ..	Gadolin.
..	CARBON.		1797	CHROMIUM ..	Vauquelin.
..	SULPHUR.		1798	GLUCINA-IUM ..	
1669	PHOSPHORUS ..	Brandt.	1802	TANTALUM ..	Hatchett.
1702	BORAX-ON ..	Homburg.	1803	CELESTINE ..	Klaproth.
1733	ARSENIC ..	G. Brandt.	"	PALLADIUM ..	Wellaston.
"	COBALT ..		"	RHODIUM ..	
1741	PLATINUM ..	Woods.	1811	IRIDIUM ..	De-cotils & Smith-
1751	NICKEL ..	Cronstedt.	1811	OSMIUM ..	son Tennant.
			1817	IODINE ..	Courtois.
			"	LITHIUM ..	Arfwedson.
			"	SELENIUM ..	Berzelius.
			1818	CADMIUM ..	Stromeyer
	SODA-IUM ..	Duhamel.	1826	BROMINE ..	Balard
1736	POTASH ..	Marggraf.	1828	THORIUM ..	Berzelius.
to	LIME ..		1830	VANADIUM ..	Sefstrom.
1758	SILEX ..	Bergmann,	1839	LANTHANUM ..	
	ALUMINA ..	and	1841	DYDIUM ..	Mosander
	MAGNESIA ..	Scheele.	1843	ERBIIUM ..	
			1844	RUTHENIUM ..	Claus.
1766	HYDROGEN ..	Cavendish.	1846	NIOBIIUM ..	H. Rose.
1771	FLUORINE ..	Scheele.	1859	CALSIUM ..	Bunsen.
1772	NITROGEN ..	Rutherford.	"	RUBIDIUM ..	
1774	CHLORINE ..	Scheele.	1861	THALLIUM ..	Crookes.
"	OXYGEN ..	Priestley.	1863	INDIUM ..	Reich and Richter.

The successive recognition of the elementary gases, quickly following Black's remarkable discovery of carbonic acid gas, began with the identification of hydrogen by Cavendish in 1766. This was succeeded by the discovery of nitrogen by Rutherford in 1772; of chlorine and fluorine acid, the latter now held to be a fluoride of hydrogen, by Scheele in 1774; and of oxygen by Priestley in the same year.

Thus prior to the discovery of the first of the elementary gases, twenty-three kinds of solid matter, and one liquid body, mercury, were known, which afterwards became recognized as elements. Between then and the present time, thirty-three kinds of solid matter, and one liquid body, bromine, have been added to the list—the discovery of the earliest of them occurring almost simultaneously with, or even just preceding, that of the last discovered of the elementary gases.

Among the number of bodies discovered prior to 1808, when Davy effected the decomposition of the alkalis, several, at first

thought to be elementary, are now known to be compounds of oxygen with other bodies still regarded as elements; and conversely, two bodies, namely, chlorine and fluorine, at one time thought to be oxides, have since become regarded as elementary; but in none of these cases did the discovery of what is now considered to be the real constitution of the bodies add or subtract an element to or from the list.

From the period of the modern or Lavoisierian conception of elements and compounds down to the beginning of the nineteenth century, the recognition of new elements occurred with much frequency, at short but varied intervals. After then, the discoveries became somewhat less frequent; but even within the last fifty years no fewer than twelve new elements have been added to the list, being at the rate of one new element every four years. Throughout, the periods of discovery have been somewhat irregular in their occurrence. Thus in the years 1802 and 1803, six new elements were discovered, namely, tantalum, cerium, palladium, rhodium, iridium, and osmium; within the succeeding fourteen years only one new element, but that a very important one, namely, iodine; and in the fifteenth and sixteenth years, three new elements, namely, lithium, selenium, and cadmium. The longest barren interval, one of thirteen years' duration, took place between the discovery of niobium, by Rose, in 1846, and that of cesium and rubidium, by Bunsen, in 1859. The last discovered of the elements, namely indium, being fully seven years old, and there being no reason to consider our present list as anything like complete, or to apprehend any cessation of additions thereto, it is now quite time for some other new element to be made known. For we may reasonably anticipate the discovery of new elements to take place at irregular intervals possibly for centuries to come, and our list of the elements to be increased at least as much in the future as in the past.

The fresh discovery, however, of any abundant elementary constituent of the earth's crust would seem scarcely now to be expected, seeing that of the thirty-two elements which have become known since the year 1774,—the year of the discovery of chlorine and oxygen and manganese and baryta, the great majority belong to the class of chemical curiosities; while even the four or five most abundant of the since discovered elements are found to enjoy but a sparing although wide distribution in nature, as is the case, for example, with bromine and iodine; or else to be concentrated but in a few specially localized minerals, as is the case, for example, with strontium and chromium, and tungsten. Of course it is difficult to appraise the relative abundance in nature of different elements; more especially from the circumstance of those which are put to commercial uses being everywhere sought for, and those not put to commercial uses being habitually neglected,—save indeed by the man of science, to whom the peculiar properties of some of the less familiarly known

elements, as palladium, osmium, erbium, didymium, uranium, and thallium, render them objects of the highest interest.

A very notable point with regard to the last-discovered four elements, namely, rubidium, caesium, thallium, and indium, is their successive discovery within a few years of each other, by one and the same process, namely, that of spectrum analysis. This process, invented and made available as a means of chemical research by Bunsen and Kirchhoff in 1859, consists simply in allowing the light given off by different ignited gases and vapours, limited by means of a fine slit, to pass through a prism or succession of prisms; and in observing the so-produced, brightly-coloured, widely-extended image of the slit. It has been known from the days of Newton, that by the passage of heterogeneous light through a prismatic highly-dispersive medium, its differently refrangible constituents become widely separated from each other, so as to furnish an elongated coloured spectrum. But whereas the spectra of incandescent solid and liquid bodies are continuous, and not distinctive of the particular luminous bodies yielding them, the spectra of incandescent gaseous or vaporized bodies are found to be discontinuous, and to consist of one or more bright lines of different colour, thickness, and position, according to the nature of the particular incandescent gases or vapours from which the light through the slit is proceeding. In this way it is found that the spectra of the different chemical elements, alike when free and in combination, are perfectly definite, and characteristic of the particular elements vaporized and made incandescent.* And in many cases, the spectra or portions of the spectra of particular elements, even when present in the most minute proportion, are so extremely well marked and distinctive, that the presence or absence of these elements is determinable with the greatest ease and certainty, by a mere inspection of the emission spectra yielded by the incandescent gases or vapours under examination. Moreover, gases and vapours are further capable of affecting heterogeneous light which is passed through them; and of thus yielding absorption spectra, in which the characteristic lines of the above-described emission spectra are reversed, so as to appear, unaltered in position, as black lines or intervals in an otherwise continuous band of colour.

Now the salts of the alkali-metals, lithium, sodium, and potassium, and certain of the salts of the alkaline-earth metals, calcium, strontium, and barium, being very readily volatile, upon heating these salts, in the non-luminous flame of a Bunsen gas-burner for example, they undergo vaporization, and their vapours become incandescent and capable of yielding the characteristic emission spectra of the particular metals. In examining in this way the alkali-salt residue of a

* For some qualifications of this statement, *vide* Roscoe's 'Spectrum Analysis.'

mineral water from Durkheim, Bunsen observed in the spectrum before him certain coloured lines not belonging to any one of the then known alkalies, potash, soda, or lithia; and yet necessarily belonging to some substance having the general characters of an alkali, since all other bodies than alkalies had been previously removed from the residue under examination. In full reliance upon the certainty of this conclusion, Bunsen evaporated some forty tons of the water in question; and from the alkali-salt residue, succeeded in extracting and separating salts of two new alkali-metals, each characterized by a well-marked pair of lines in the blue or indigo, and one of them having in addition a pair of well-marked lines of extremely small refrangibility in the red of the spectrum. From its yielding these red lines, the one metal was named rubidium; the other, of which the bright blue lines were especially characteristic, being called cesium.

The very general distribution in nature of these two elements was speedily established, and salts of each of them were, with much labour, eventually prepared in a state of purity and in reasonable quantity. From certain of their respective salts the metals themselves were obtained by the usual processes, and together with their salts, were submitted to detailed chemical examination. And no sooner was this examination made, than the position of the newly-discovered elements, as members of the alkali-metal family, at once became apparent. Rubidium and cesium were found in all their properties to present the most striking analogy to potassium, and evidently to stand to this metal in the same relation that strontium and barium respectively stand to calcium; while they differed from sodium, much as strontium and barium respectively differ from magnesium. This relationship in obvious properties was further borne out by the relationship of their atomic weights, thus:—

Mg	24	Na	23	F	19	O	16
{ Ca	10	{ K	39	{ Cl	35.5	{ S	32
{ Sr	87	{ Rb	85	{ Br	80	{ Se	79
{ Ba	137	{ Cs	133	{ I	127	{ Te	129

It is observable that the sequence of atomic weight in the thus completed alkali-metal family, is strictly parallel to the previously well-known sequences in the alkali-earth metal family, and in the halogen and oxygen families respectively. Moreover, just as the basylity of the alkaline-earth metals increases in the order of their several atomic weights - calcium being less basylous than strontium, and far less basylous than barium - so also is the basylity of potassium inferior to that of rubidium, and the basylity of rubidium inferior to that of cesium, which is indeed the most powerfully basylous, or oxidizable, or electro-positive element known.

Since 1860, both rubidium and cesium have been recognized as minute constituents of a considerable number of minerals and mineral

waters, rubidium having been met with for the most part in a larger proportion by weight than cæsium. Unlike potash, originally known as vegetable alkali, cæsium has not been recognized in the vegetable kingdom; but rubidium has been found as a very common minute constituent of vegetable ashes, as those of beetroot, oak-wood, tobacco, grapes, coffee, tea, &c. On the other hand, cæsium, free from rubidium, has been found in a tolerably well-known, though rare, mineral from the Island of Elba, to the extent of 32 per cent. by weight of the mineral. The history of this mineral is curious: from the circumstance of its always occurring in association with another mineral, a variety of petalite, the two were called Castor and Pollux. Castor was found to be substantially a silicate of alumina and lithia; pollux a silicate of alumina, and, as it was thought, of potash. The constituents of pollux, namely, silica, alumina, and potash, with small proportions of ferric oxide, lime, soda, and water were duly estimated; but the quantities of these constituents, found in 100 parts of the mineral, instead of amounting to 100 parts or thereabouts, amounted only to 88 parts, there being somehow a loss of 12 per cent. in the analysis. After Buusen's discovery of the new alkali-metals, pollux was analyzed afresh by Pisani, who soon perceived that what had formerly been taken for potash, and estimated as potash, was not potash at all, but cæsia. Then calculating out his own analysis with cæsia instead of potash, substituting the one for the other in the proportion of $133 + 8$, or 141 parts of cæsia, for $39 + 8$, or 47 parts of potash, he found that the quantities of the different constituents furnished by 100 parts of the mineral yielded by their addition the full sum of 100 parts required.

In submitting to spectroscopic examination a certain residue left by the distillation of some impure selenium, Mr. Crookes, early in 1861, recognized in the spectrum before him a brilliant green line, from which he inferred the presence in the above residue of a new element; and by the end of the same year, he had succeeded in establishing the tolerably wide distribution of this element, to which he gave the name of thallium; in procuring it, though but in small quantity, in a separate state; and in satisfying himself of its metallic character. Soon afterwards, and without knowledge of Mr. Crookes' later results, the metal was obtained by M. Lamy on a comparatively large scale, and was exhibited by him in the form of small ingots at the London Exhibition of 1862. He procured it from the fine dust met with in some oil of vitriol factories, as a deposit in the flues leading from the pyrites burners to the leaden chambers. In these deposits, the minute proportion of thallium contained originally in the pyrites becomes concentrated, so as to form in some instances as much as 8 per cent. by weight of the dust. Independently, moreover, of its occurrence in iron pyrites, thallium, though never forming more than a minute constituent of the different minerals and mineral waters in which it occurs, is now known to be capable of extrac-

tion from a great number and variety of sources. But from no other source is it so advantageously procurable as from the above-mentioned fine deposit; and so early as the autumn of 1863, at the meeting of the British Association in Newcastle, the then mayor, Mr. J. Lowthian Bell, exhibited several pounds, and Mr. Crookes no less than a quarter of a hundredweight of thallium obtained from this comparatively prolific source. In one respect, the discovery of thallium presented even a greater degree of interest than attached to the discovery of cæsium and rubidium. For whereas these two elements were at once recognized as analogues of the well-known metal potassium, thallium can hardly be said, even at the present time, to be definitely and generally recognized by chemists as the analogue of any particular metal, or as a member of any particular family of elements. With each of such differently characterized elements as potassium, lead, aluminum, silver, and gold, it is associated by certain marked points of resemblance; while from each of them it is distinguished by equally well-marked points of difference. Hence the necessity for subjecting thallium and its salts to a thorough chemical examination, so as to accumulate a well-ascertained store of facts with regard to it. And thanks to the careful labours of many chemists, more particularly of Mr. Crookes in London, and of Messrs. Lamy and Willm in Paris, our knowledge of the properties of thallium and of its salts may compare not unfavourably with our similar knowledge in relation to even the longest known of the metallic elements. Still it was not until our knowledge of indium had culminated in the determination of its specific heat only last year, that the position of thallium as an analogue of indium, and a member of the aluminum family of elements became unmistakably evident.

Indium was first recognized in 1863, by Drs. Reich and Richter, in the zinc blende of Freiberg in Saxony, and by reason of the very characteristic spectrum afforded,—consisting of two bright blue or indigo bands; the brightest of them somewhat more refrangible than the blue line of strontium, and the other of them somewhat less refrangible than the indigo line of potassium. Since its first discovery, indium has been recognized in one or two varieties of wolfram, and as a not unfrequent constituent of zinc ores, and of the metal obtained therefrom, but always in a very minute proportion. Indeed, indium would appear to be an exceedingly rare element, far more rare than its immediate predecessors in period of discovery. Its chief source is metallic zinc,—that of Freiberg, smelted from the ore in which indium was first discovered, containing very nearly one-half part of indium per 1000 parts of zinc. A considerable quantity of indium extracted from this zinc, was shown in the Paris Exhibition of 1867; and an ingot from the Freiberg Museum, weighing 200 grammes, or over 7 ounces, has within the last few days been kindly forwarded by Dr. Richter himself, for inspection on the present occasion. To Dr. Schuchardt, of Goerlitz, also, the members of the Institution are

indebted for his loan of nearly 60 grammes of metallic indium; and of fine specimens of other rare chemical products, prepared with his well-known skill, in a state of great purity and beauty.

When zinc containing indium is dissolved not quite completely in dilute sulphuric or muriatic acid, the whole of the indium originally present in the zinc is left in the black spongy or flocculent residue of undissolved metal, with which everyone who has prepared hydrogen gas by means of zinc and acid is so well acquainted. Besides some zinc, this black residue is found to contain lead, cadmium, iron, and arsenic, less frequently copper and thallium, and in some cases, as that of the Freiberg zinc, a small proportion of indium. From the solution of this residue in nitric acid, the indium is separated by ordinary analytical processes, based chiefly on the precipitability of its sulphide by sulphuretted hydrogen from solutions acidulated only with acetic acid; and on the precipitability of its hydrate both by ammonia and carbonate of barium. From its soluble salts, metallic indium is readily thrown down in the spongy state by means of zinc. The washed sponge of metal is then pressed together between filtering paper, by aid of a screw press, and finally melted under a flux of cyanide of potassium.

Thus obtained, indium is a metal of an almost silver-white colour, apt to become faintly bismuth-tinted. It tarnishes slowly on exposure to air, and thereby acquires very much the appearance of ordinary lead. Like lead, it is compact and seemingly devoid of crystalline structure. Moreover, like lead and thallium, it is exceedingly soft, and readily capable of furnishing wire, by the process of "squirting" or forcing. The specific gravity of indium, or 7.4, is very close to that of tin, or 7.2; and much above that of aluminium, 2.6, and below that of lead, 11.4, and that of thallium, 11.9. In the lowness of its melting point, namely, 176° C., indium occupies an extreme position among the metals permanent in air; the next most fusible of these metals, namely tin and cadmium, melting at 228°; bismuth at 261°; thallium at 294°; and lead at 325°. Though so readily fusible, indium is not an especially volatile metal. It is appreciably less volatile than the zinc in which it occurs, and far less volatile than cadmium. Heated as far as practicable in a glass tube, it is incapable of being raised to a temperature sufficiently high to allow of its being vaporized, even in a current of hydrogen.

Indium resists oxidation up to a temperature somewhat beyond its melting point, but at much higher temperature it oxidizes freely; and at a red heat, it takes fire in the air, burning with a characteristic blue flame and abundant brownish smoke. It is readily attacked by nitric acid, and by strong sulphuric and muriatic acids. In diluted sulphuric and muriatic acids, however, it dissolves but slowly, with evolution of hydrogen. Oxide of indium is a pale yellow powder, becoming darker when heated, and dissolving in acids with evolution of heat. The hydrated oxide is thrown down from indium solutions by ammonia, as a white, gelatinous, alumina like precipitate, drying up into a horny mass. The

sulphide is thrown down by sulphuretted hydrogen as an orange-yellow precipitate, insoluble in acetic but soluble in mineral acids. The hydrate and sulphide of indium, in their relations to fixed alkali solutions more particularly, seem to manifest a feebly-marked acidulous character. Chloride of indium, obtained by combustion of the metal in chlorine gas, occurs as a white micaceous sublimate; and is volatile at a red heat, without previous fusion. The chloride itself undergoes decomposition when heated in free air, and the solution of the chloride upon brisk evaporation, with formation in both cases of an oxichloride.

But the chief point of chemical interest with regard to any newly-discovered element, and consequently with regard to indium, is the establishment of its atomic weight; which, in the case of a metallic element, is based primarily upon the determination of the ratio in which it combines with oxygen and chlorine. Now the quantity of indium which unites with 8 parts by weight of oxygen and with 35.5 parts by weight of chlorine, has been found by Winkler to be 37.9, and by Bunsen to be 37.8 parts. But this determination of combining ratio falls far short of the definite establishment of the atomic weight of the metal. For example, the quantities of silver, mercury, bismuth, tin and tantalum, which exist in the best-known chlorides of these metals combined with 35.5 parts of chlorine, are 108, 100, 70, 29, and 37 parts respectively. Nevertheless, the atomic weights of these metals are taken to be not 108, 100, 70, 29, and 37, but 108, 200, 210, 118, and 181 respectively, the chlorides of the several metals being expressed by the formulæ AgCl , HgCl_2 , BiCl_3 , SnCl_4 , and TaCl_5 , respectively. Accordingly, in order to deduce the atomic weight of indium from the ascertained composition of its chloride, we require first to know whether its chloride is a mono-, di-, tri-, tetra-, or penta-chloride. Now, in the case of a metal forming only one definite chloride, the constitution of the chloride as a mono- or poly-chloride, may frequently be determined by a consideration of the analogies presented by the metal and its compounds to some other metal and its compounds, of which the atomic weight and molecular formulæ respectively are well established. But it is obvious that analogy can afford but little help in the case of a newly-discovered element, of which the analogies have still to be determined.

Failing analogy, a more sure guide to the establishment of the molecular formula of a metallic chloride is afforded in some instances by a determination of its vapour density, - tantamount to a determination of the quantity of chlorine by weight, contained in a given volume of the gas or vapour of the chloride experimented on. Thus, having estimated the quantity of chlorine contained in a given volume of heated muriatic acid gas, the quantities of chlorine contained in the same volume of the vaporized chlorides of mercury, bismuth, tin, and tantalum, under the same circumstances of pressure and temperature, are found to be 2, 3, 4, and 5 times as great, whence the formulæ HgCl_2 , BiCl_3 , SnCl_4 , and TaCl_5 , respectively. Now indium chloride being volatile at a red heat, there is no reason, save that re-

sulting from the rarity and value of the body, why the density of its vapour should not be ascertained. As a matter of fact, however, no estimation of the vapour density of indium chloride has yet been made, and any evidence that might be deducible from it, is consequently not forthcoming.

Lastly, a most important guide to the establishment of the atomic weight of a metal is the determination of its specific heat. In cooling through the same fall of temperature, different bodies, as is well known, give out exceedingly different quantities of heat. In the case of a pound of bismuth and a pound of brass for instance, both raised to the temperature of boiling water, and then immersed in an excess of ice, the quantity of ice melted by the pound of brass in cooling down to the freezing point, will be found to be more than three times as great as the quantity of ice melted by the pound of bismuth. Now the determination of the specific heats of most of the metals, compared with the specific heat of an equal weight of water as unity, has been made with extreme care and exactitude by Regnault; and on looking at the following list of specific heats, mostly of his determination, it is evident, almost at a glance, that the specific heats of the metallic elements are inversely as their respective atomic weights. Thus, taking the first and last elements on the list for example, it is observable that the specific heat of lithium, or 0.94, is weight for weight thirty times greater than the specific heat of bismuth, 0.03; but then the atomic weight of bismuth is thirty times greater than that of lithium. And throughout, the product of the specific heat into the atomic weight of one metal, divided by the product of the specific heat into the atomic weight of another metal, is approximatively equal to 1, as shown in the fourth column of the following Table, in which the product of the specific heat into the atomic weight of silver is taken as the standard dividend. Now, only last year, concordant estimations of the specific heat of indium were made by Bunsen and a Russian chemist, Mendelejeff; the mean of Bunsen's two estimations being 0.0569, which it will be observed is very close to Regnault's estimations of the specific heats of silver, cadmium, and tin. Accordingly, the atomic weight of indium must approximate to the atomic weights of silver, cadmium, and tin; or, in other words, it cannot be 37.8×1 , or 37.8×2 , but must be $37.8 \times 3 = 113.5$; and the quantity of chlorine combined with this weight of indium being three times 35.5 parts, indium chloride will necessarily appear as a trichloride, and be expressed by the formula InCl_3 . The determination of specific heats being a matter of direct experiment, with scarcely any ratiocination whatever, it seems impossible for anyone to observe the relationship subsisting between the accepted atomic weights of the metals, deduced from experiment by a highly complex train of reasoning, and their directly ascertained specific heats, without recognizing that in the case of the metals, at any rate, the atomic weights of the chemist are something more than vain imaginings, but that they are beyond question the terse expression of a fundamental truth in nature.

TABLE II.—ATOMIC HEATS OF METALS

Chlorides.	Atomic Weights.	Metals	Specific Heats	Atomic Heats.
Li Cl	7	Lithium	·9408	1·07
Na Cl	23	Sodium	·2934	1·09
Mg Cl ₂	24	Magnesium .. .	·2499	0·97
Al Cl ₃	27·5	Aluminum	·2143	0·95
K Cl	39	Potassium	·1695	1·07
Ca Cl ₂	40	Calcium	·1686	1·09
Mn Cl ₂	55	Manganese	·1217	1·08
Fe Cl ₂ , Fe Cl ₃ .	56	Iron	·1138	1·03
Ni Cl ₂	59	Nickel	·1075	1·03
Co Cl ₂	59	Cobalt	·1067	1·02
Cu Cl, Cu Cl ₂ .	63·5	Copper	·0955	0·98
Zn Cl ₂	65	Zinc	·0955	1·01
As Cl ₃	75	Arsenic	·0814	0·99
Mo Cl ₄	96	Molybdenum .. .	·0722	1·12
Ru Cl ₃ , Ru Cl ₄ ..	104	Ruthenium . . .	·0611	1·03
Rh Cl ₃	104	Rhodium	·0580	0·98
Pd Cl ₂	106	Palladium	·0593	1·02
Ag Cl	108	Silver	·0570	1·00
Cd Cl ₂	112	Cadmium	·0567	1·03
In Cl ₃	113·5	Indium	·0569	1·05
Sn Cl ₂ , Sn Cl ₄ ..	118	Tin	·0562	1·07
Sb Cl ₃ , Sb Cl ₅ ..	122	Antimony	·0508	1·00
Te Cl ₄	129	Tellurium .. .	·0471	1·03
W Cl ₄ , W Cl ₆ ..	184	Tungsten	·0334	1·00
Au Cl, Au Cl ₃ ..	196·5	Gold	·0325	1·03
Ir Cl ₃ , Ir Cl ₄ ..	197	Iridium	·0326	1·04
Pt Cl ₂ , Pt Cl ₄ ..	197	Platinum	·0324	1·04
Os Cl ₂ , Os Cl ₄ ..	199	Osmium . . .	·0311	1·00
Hg Cl, Hg Cl ₂ ..	200	Mercury	·0319	1·03
Tl Cl, Tl Cl ₃ ..	203	Thallium	·0325	1·07
Pb Cl ₂	207	Lead	·0314	1·05
Bi Cl ₃	210	Bismuth	·0308	1·05

The most important chemical characters of indium being thus established, there remains for consideration only the question of its affinities to certain of the previously-known elements. And seeing that the atomic weights of the elements range from 1, the atomic weight of hydrogen, up to 240, the atomic weight of uranium, there opens out the further question, whether the more obvious chemical properties of the different elements are seriated in any way with their atomic weights; or to put this last question in another form, whether the varied chemical properties of the elements are distributed among them haphazard, or according to some definite system of which the relationship subsisting between their several atomic weights may possibly serve as a key. Now the atomic weights, as distinguished from the combining proportions, of yttrium, erbium, cerium, lanthanum, and didymium, must be regarded for the present as quite unknown. Out of the fifty-eight elements, however, of which the atomic weights have been more or less well determined, forty-six have their several atomic weights ranging from 1 to 137, in an almost unbroken succession. Ten of the other twelve have atomic weights ranging from 184, that of tantalum, to 210, that of bismuth; while the remaining two,

TABLE III.—ELEMENTS, IN ORDER OF ATOMIC WEIGHT.*

1.	2.	3.	4.	5.	6.	7.	8.	Type
I. H 1	Li 7	Na 23	K 39	..	Rb 85	Ag 108	Cs 133	R Cl
II.	G 9	Mg 24	Ca 40	Zn 65	Sr 87.5	Cd 112	Ba 137	R Cl ₂
III.	B 11	Al 27.5	X ^a	In 113	Y ^b	R Cl ₃
IV.	C 12	Si 28	Ti 50	..	Zr 89	Sn 118	X ^c	R Cl ₄
V.	N 14	P 31	V 51	As 75	Nb 94	Sb 122	..	R Cl ₅
VI.	O 16	S 32	Cr 52.5	Se 79	Mo 96	Te 129	..	R Cl ₆
VII.	F 19	Cl 35.5	Mn 55	Br 80	..	I 127	..	R Cl ₇
VIII.	Fe 56 Co 59 Ni 59	..	Ru 104 Rh 104 Pd 106	R Cl ₈
	Ni 23	..	Cu 63.5	..	Ag 108			

namely, thorium and uranium, have the closely-approximating atomic weights 238 and 240 respectively. In the above Table, the symbols of the forty-six elements having atomic weights ranging from 1 to 137,

* This Table is based on one published by the author in 1861-5. Similar tables have been constructed by Newlands, Meyer, Mendelejeff, and others. The positions marked X^a, X^b, and X^c, are assigned by Mendelejeff to yttrium, didymium, and cerium, respectively. The recognition of the atomic weight of uranium as 240, is also due to Mendelejeff.

are set down in the order of the atomic weights of the elements symbolized,—save only in the case of tellurium, of which the symbol is placed immediately above, instead of below that of iodine, and of which the atomic weight may not improbably have been somewhat over-estimated. And violating the order of numerical seriation in this small particular only, it is remarkable with what facility the symbols of the forty-six elements may be arranged in parallel lines and columns, corresponding to a natural classification of the elements themselves into analogous groups and series. Indeed, a study of the entire number of elements at present known, would seem to indicate that they are one and all associated with each other by a certain community of relationship; of which the well-known gradation and parallelism in properties and atomic weights, of the members of the alkali and earth-alkali, and of the halogen and oxygen families of elements afford only the most prominent examples.

Taking the second line of the Table as an illustration, it is observable that the seven metals symbolized thereon are distinguished from all the others by their common property of forming one chloride only, and that a di-chloride; further, that the metals figuring in the uneven-numbered columns of this line, namely, magnesium 24, zinc 65, and cadmium 112, are permanent in the air, are volatilizable in the direct, and basyous in the inverse order of their atomic weights, and are otherwise specially associated with one another; while the similarly associated metals of the alternate or even-numbered columns, namely, calcium 40, strontium 87·5, and barium 137, are quickly oxidizable in the air, are practically non-volatile, and are basyous in the direct instead of in the inverse order of their atomic weights; and similarly, on the other lines of the Table, the elements symbolized are divisible into sub-groups, according to their odd and even positions respectively.

Such being the relationship of the elements placed on the same line, the relationship of those in the same column is of a different kind. Taking the third and seventh columns by way of illustration, it is observable that the consecutive elements in each column have closely consecutive atomic numbers; that the element on the first line forms a mono-chloride; that on the second line, a di-chloride; that on the third line, a tri-chloride; and that on the fourth line, a tetra-chloride; while those on the fifth, sixth, and seventh lines form oxides or oxichlorides, corresponding to a penta-, hexa-, and hepta-chloride respectively.

By reason of its atomic weight, 113·5, indium is observed to figure on the third line and seventh column of the above Table; but its position among the elements is better recognizable by a glance at the Table below, containing a portion only of the preceding one, supplemented by an additional column of elements of higher atomic weight than any of those included previously.

In respect of its atomic weight, then, triad indium occupies a position exactly intermediate between the positions of diad cadmium and tetrad tin, to both of which metals it presents a most marked re-

semblance in properties. They all three have the same extreme degree of fusibility, and much the same oxidizability and reducibility. Their sulphides are alike characterized by a yellow colour, that of cadmium, CdS , being neutral; that of tin, SnS_2 , being acidulous; and that of indium, In_2S_3 , being strictly intermediate.

	3.	7.	10.	Type.
I.	Na 23	Ag 108	..	R Cl
II.	Mg 24	Cd 112	Hg 200	R Cl ₂
III.	Al 27·5	In 113·5	Tl 203	R Cl ₃
IV.	Si 28	Sn 118	Pb 207	R Cl ₄
V.	P 31	Sb 122	Bi 210	R Cl ₅
VI.	S 32	Te 129	..	R Cl ₆

Viewed in another aspect, triad indium occupies a position intermediate between the positions of its remote triad congeners, aluminium and thallium. The mean atomic weight of the three metals being 114·3, the atomic weight of indium is 113·5. The mean specific gravity of the three metals being 7·3, the specific gravity of indium is 7·4. And in respect of purely chemical habitudes, hydrated alumina and hydrated india might easily be mistaken for one another. It is interesting, moreover, to remark that the last-discovered two metals indium and thallium—discovered, it will be remembered, by the same process, that of spectrum analysis—should bear to one another much the same sort of relation that is borne to one another by the jovian and saturnine metals of the alchemical or even pre-alchemical era. Just, for example, as the unstable and least-known chloride of lead, PbCl_2 , corresponds to the stable chloride of tin, SnCl_4 , so does the unstable and least-known chloride of thallium, TlCl_3 , correspond to the stable, and as yet only known, chloride of indium, InCl_5 , as suggested, indeed, by the lecturer some six or seven years ago.

The study of such relationships necessarily suggests many inquiries. Arranging the entire fifty-eight elements of which the atomic weights are known, in a table similar to the preceding one for the forty-six elements having atomic weights not exceeding 137, some twenty or five-and-twenty new elements would be required to fill up the gaps in the different series; but why should not new elements be discovered having atomic weights as much above that of uranium, 240, as its atomic weight is above that of barium, 137?

Again, does it seem probable that bodies capable of being arranged in such a well-marked numerical series, are really elementary and mutually independent; or is it more likely that the gradation of properties and atomic numbers manifested by these bodies, depends on their possession of different increments of common material?

May it not be that the numerical ratio between the atomic numbers of proximate elements, $\frac{x}{y} = \text{approximately } \frac{y}{x}$, is really absolute; and that it will hereafter be proved to be so by a better determination of atomic weights. Seeing that a short time back, caesium with the atomic weight 133, and rubidium with the atomic weight 85, both occurred as unrecognized impurities in potassium with its atomic weight 39, who shall answer for the absolute accuracy of even the best established of our present atomic weights?

Again, the mean difference in atomic weight between consecutive analogous elements, is, in the case of the nine following pairs of elements, lithium and sodium, glucinum and magnesium, boron and aluminum, carbon and silicon, nitrogen and phosphorus, oxygen and sulphur, fluorine and chlorine, sodium and potassium, magnesium and calcium, 16.1; the lowest difference being 15, and the highest 17. The mean difference in the case of the four following similar pairs of proximate elements, phosphorus and vanadium, sulphur and chromium, chlorine and manganese, arsenic and niobium, is 19.25; the lowest difference being 19, and the highest 20.5. Lastly, the mean difference in the case of the seven following similar pairs of proximate elements, calcium and zinc, vanadium and arsenic, manganese and bromine, rubidium and silver, strontium and cadmium, silver and caesium, tantalum and bismuth, is 24.6; the lowest and highest differences, even in the case of these elements of such high atomic weight, being 23 and 26 respectively. Are these differences in atomic weight only approximatively, or are they indeed absolutely, 16, 20, and 24 respectively; and if so, why should the numerical difference between proximate associated elements be 16 in one set of cases, 20 in another set, and 24 in a third?

[W. O.]

Friday, February 2, 1872.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

PROFESSOR TYNDALL, LL.D. F.R.S.

On the Identity of Light and Radiant Heat.

WHETHER we regard its achievements in the past, or its promise and tendency in the future, all that we know of physical science—every bent and bias which we receive from its pursuit—tends to confirm the dictum of the poet regarding this universe:—

“All are but parts of one stupendous whole,
Whose body Nature is.”*

If I halt here, and omit the next clause of the couplet, it is not because physical science has arrived at any conclusion hostile to that clause, at all events in its profoundest signification, but simply because what the poet goes on to affirm lies outside the sphere of science. We, as physical students, have to do with “Nature” only, and our view of nature could not be more happily expressed than by the figure employed by the poet. For our vocation, and the delight and discipline that it confers, do not consist in the registration of unrelated facts and phenomena; but in the searching out and discovery of relationship in a system, whose parts we hold to be as closely and definitely related to each other as are the various organs and functions of the living body itself.

It was this spirit of search, this capacity and desire, developed amid natural agencies, to detect the lines of connection between these agencies, that gave for a time such keen interest to the discussion, whether light and heat were essentially different things, or whether a substantial identity subsisted between them. It is not so very many years since that most excellent experimenter and philosophical inquirer, Melloni, isolated from a solar beam a brilliant light, and finding it incompetent to affect his most sensitive thermoscopic apparatus, concluded that light and heat were essentially distinct. But in drawing this conclusion, Melloni forgot that he was implicitly dealing with an instrument of almost infinitely greater delicacy than his thermoscopic apparatus; he forgot that the human eye, and the consciousness connected with the eye, are capable of being vividly excited by an amount of force which when translated into heat might

* “All are but parts of one stupendous whole,
Whose body Nature is, and God the soul.”

Pope's *Essay on Man*, Epistle I, line 267.

defy all the thermometers in the world to detect it. Melloni himself subsequently modified his conclusion.

It is not so very long since the late Principal Forbes was eagerly engaged in establishing the important point that radiant heat, like light, is capable of being polarized. Since that time Knoblauch, Foucault, Fizeau, and Seebeck have applied their refined experimental skill to this question of identity; and those excellent investigators De la Provostaye and Desains, pushed the analogy between light and heat so far as to prove that the magnetization of a ray of light, in Faraday's sense of the term, has its parallel in the magnetization of a ray of heat.

It was, however, in their private cabinets that these experimenters obtained their results, which were in most cases so small, as to require attention on the part of a skilled observer to detect them. But science grows, and our experimental means augment as our knowledge expands. Recent discoveries and improvements will, I trust, enable me to make evident to you, to-night, effects which have been hitherto confined to far more limited circles; some of which indeed have only been seen by the observers who first noticed and described them. And if those accidents which often hold sway over lecture-experiments of a delicate character should prove favourable, we may be able to push the subject a hair's breadth beyond the limits which observation has hitherto assigned to it.

Heat is presented to us in two aspects: sometimes associated with ordinary matter, through which it creeps by the process of conduction; sometimes not associated with ordinary matter, but, like light, flying through space with immense velocity. In this latter form it is called *radiant heat*. Radiant heat obviously and palpably comes to us from the Sun, but here it is entangled with light. Let me, in the first place, endeavour to unravel this entanglement.

When white light is refracted, it is unravelled and the spectrum is produced. A spectrum of the electric light was thrown upon a screen; and red, green, and black ribbons about an inch wide were successively moved along it. The red placed in the red light appeared a brilliant red; when moved into the green it became black. In like manner the green ribbon moved from the green, where it shone vividly green, into the red, became an intense black. The black ribbon was black in every part of the spectrum.

Now the red ribbon is not heated in red, and the green is not heated in green; but red is heated in green, and green in red. We have heating only where we have absorption; and the heat generated is the equivalent of the light absorbed. Black absorbs all the rays of light, hence, indeed, its blackness; and if it could speak, it might tell us the warmth of every colour. But warmth exists outside the colours. Beyond the red, where nothing is seen, the force acting on the retina is far greater than when the eye is plunged in the red. The objective here is entirely out of proportion to the subjective.

The existence of this heat was thus proved. All the colours but

the red were cut off by a red glass, and with a diaphragm having a circular opening, a well-defined red circle was produced. This was refracted by a prism, still remaining a circle. A thermo-pile with its face towards the lamp was then caused to approach the path of the beam. It would have been seen by its shadow on the screen if the light had been at all invaded; but with a considerable interval between the pile and the light, a large deflection of the galvanometer testified to the presence of heat beyond the luminous circle. An opaque solution* was substituted for the red glass. A circle remained, but it was an invisible circle of radiant heat instead of a circle of light, and the needle of the galvanometer did not fall, though the visible image had vanished.

Thus, as regards refraction, we have radiant heat behaving like light. And now for reflexion. A horizontal beam of light was reflected upwards by a plane mirror, and when the light was cut off by the introduction of the opaque cell, a powerful beam of reflected heat was proved still to remain. The luminous beam was then *totally reflected* by a prism to a horizontal direction; the light was again cut off, and a powerful deflection of the galvanometer needle was obtained by the residual heat-beam. Thus, in respect to common and total reflexion the behaviour of light and heat is the same.

The action of lenses on light and heat was then demonstrated, the invisible heat-rays being brought to a focus as readily as the rays of light.

A beam of light was then made to strike a concave mirror, and at the focus, which was strikingly visible in the dust of the room, the thermo-pile was placed, having its face covered. The light being cut off by the dark cell, and the covering screen drawn away, the needle of the galvanometer at once flew to its stops.

Double refraction by Iceland spar was next described and explained. It was illustrated by passing through the spar a circular beam of light, which, on the screen, gave two images. The places on the screen where these two images fell were marked, and the light was cut off by the iodine cell. On introducing the thermo-pile with its face towards the lamp, when it occupied the position of either light-image, a deflection of the needle was obtained. Of the two images, one is the ordinary, the other the extraordinary. Is the same true of the heat? Placing the pile in the place of the ordinary image, cutting off the light, and turning the spar, the deflection of the needle remained unchanged; but when the spar was turned round, while the pile occupied the place of the extraordinary image, the needle instantly fell. Why? Removing the dark cell and rotating the spar, the extraordinary light-image was seen to rotate round the ordinary one, which remained fixed. The heat-beam did the same and thus quitted the pile. Here then we prove that the heat-beam also

has its ordinary and extraordinary image. This, it was believed, was the first time the effect had been obtained with purely invisible heat. Knoblauch had demonstrated the double refraction of heat, using the total beam, luminous and non-luminous, of the Sun.

Some of the phenomena of polarization were next touched on. Light is propagated by the undulations of an etherial medium, the direction of vibration being perpendicular to the direction of propagation. A crystal of tourmaline has the property of quenching all vibrations except those which are parallel to the axis of the crystal; hence, a plate of tourmaline cut parallel to the axis will allow all vibrations in that direction to pass through it, but will stop all others. A beam of light which has passed through one plate of tourmaline is therefore unable to pass through another placed transversely to it, whereas, if the axes are parallel, the light is but little dimmed by the second plate. The black space due to the superposition of the crossed plates of tourmaline was shown, as also the abolition of the darkness by a thin film of mica introduced between the plates.

A beam with all its vibrations reduced to the same plane is called a beam of *plane polarized light*.

The two beams emergent from double-refracting spar are thus polarized. Nicol got rid of one. He cut a parallelepiped of spar into two by a very oblique section, polished the two surfaces, and united them by Canada balsam. The ordinary or more powerfully refracted ray, at the surface of the balsam is, in consequence of its obliquity, totally reflected, and the extraordinary ray passes on alone. In this way we obtain an intense beam of polarized light.

A beam of light was sent through two large Nicol prisms, and shown to be entirely extinguished when the principal sections of the prisms crossed each other. The introduction of a plate of mica between them caused, as in the case of the crossed tourmalines, the instant reappearance of the light. The opaque cell was then placed in front of the lamp, all visible rays being thus intercepted. The thermo-pile was next placed so as to receive the beam after leaving the second Nicol prism. Causing one of the crossed prisms to rotate, a path was opened for the heat exactly as for the light, the deflection of the needle speedily bearing witness to the fact. The prisms being again crossed, the heat-beam was again quenched; but as in the case of light, the introduction of a piece of mica restored the heat and caused a large deflection of the galvanometer.

Faraday's great experiment was next performed. A beam of light, polarized by one Nicol's prism, was made to pass through a piece of heavy glass placed between the perforated poles of an electro-magnet, and afterwards through another Nicol, so placed that the beam was extinguished. When the magnet was excited the plane of polarization was caused to rotate and a luminous image flashed instantly out upon the scene.

The effect of magnetization is greatly augmented by adopting the device of MM. De la Provostaye and Desains, of causing the principal

sections of the Nicol's prism to enclose, not a right angle, but an angle of 45° . This was done, the heat falling on the pile being neutralized by the method of compensation. On sending a current round the magnet a considerable deflection of the needle was obtained, the direction of the deflection depending on that of the magnetizing current.

De la Provostaye and Desains thus obtained with luminous solar heat a deflection of two or three degrees. With the iodine filter and the electric lamp a deflection equivalent to 150 of the lower degrees of the galvanometer was obtained from purely non luminous heat.

[J. T.]

Friday, February 16, 1872.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

JOHN HALL GLADSTONE, Esq. Ph.D. F.R.S. F.C.S. M.R.I.

On the Crystallization of Silver, Gold, and other Metals.

THERE are few chemical experiments so well known as the growth of the "lead tree," a specimen of which is on the table, together with a "silver tree" that is said to have been made by the late Professor Faraday. These carry our minds back to the time of the alchemists, who called the first "arbor Saturni," and the second "arbor Dianæ;" and they may be looked upon as the types of a large number of phenomena, in which the salt of one metal in solution is decomposed by some other metal. My assistant, Mr. Tribe, and myself have been lately examining these replacements, the metallic crystals which are thus produced, and the forces that act through the liquid.

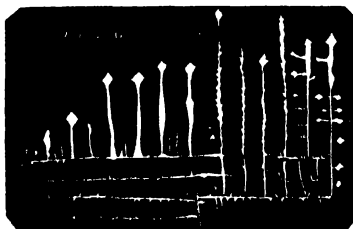
Our more special attention has been given to the mutual action of copper and nitrate of silver. If these two substances be brought into contact by the intervention of water, there grow upon the red metal what may be well called "trees," and though the analogy between crystals and plants is a very superficial one, yet the resemblances of external form are striking enough, and a nomenclature drawn from the garden seems the most expressive.

It is very beautiful to watch the growth of these silver crystals round a piece of copper under the microscope; a blue glass underneath adds to the effect, and they are best seen when they reflect a strong light thrown upon them. They may be also thrown upon a screen as opaque objects, but the beauty and lustre of their surface is in this way lost.

The crystals of silver thus produced differ both in colour and form, according to the strength of the solution. If it be very weak—say one per cent.—the copper is fringed with black bushes of the metal, which, in growing, change their colour to white without any alteration of crystalline form that can be detected by a powerful microscope. A stronger solution gives white crystals from the commencement, which frequently assume the appearance of fern-leaves; while the growth from a still stronger liquid reminds us rather of a furze bush. If the nitrate of silver amount to 15 per cent., or thereabouts, there occurs a steady advance of brilliantly white moss; and if the solution be saturated, or nearly so, say 40 per cent., this moss

is very sturdy, often ending in solid crystalline knobs, or stretching out into the liquid as an arborescent fringe.

In all these cases, however, when the solution in front of the growing crystals has been somewhat exhausted, certain prominent or well-circumstanced crystals seem to monopolize the power, and to push forward through the remaining portions of the liquid. This gives rise to beautiful branches which assume a variety of graceful forms, which it is hopeless to attempt to portray by diagrams, but of which the subjoined figures give some of the more characteristic outlines greatly magnified. The weak solutions produce feathery crystals somewhat as in Fig. 1, consisting of a straight central stem



from which grow on either side crystalline rays that terminate in a sharp point, and frequently become themselves the centre stems of a similar crystalline structure. In the outlying growth of a moderately strong solution the apparent regularity of the crystalline form is lost; the main stem is built up of a confused mass of hexagonal plates, while the side branches are an agglomeration of minute pointed crystals turning in every direction, and producing such jagged outlines as are drawn in

Fig. 2. In stronger solutions still the branches lose every appearance of straightness, and they are built up of hexagonal plates so studded with crystalline specks that the whole has the rounded appearance depicted in Fig. 3. The arborescent crystals that succeed the fringes from a saturated solution, are smaller in their foliage than the last, and end in little spherical or botryoidal knobs.

Beside these various forms, there occur all kinds of crystalline combinations, as, for instance, the spray sketched in Fig. 4, where the rough branches have terminated each in a large hexagonal plate, and the flowing past of a weakened solution has afterwards caused the growth of delicate fern-leaves. Often, too, a large expansion will take place in every direction, though joined to the parent stem by an almost invisible thread; or from the point of a long crystal there will branch out to right and left crescent-shaped structures, a process the commencement of which is seen in one of the side rays of Fig. 1. The last traces of silver in the liquid will frequently give rise to delicate crystalline filaments wandering over the surface of the glass, as in Fig. 5.

If a piece of zinc be placed in a solution of neutral terchloride of gold, containing about 9 per cent. of salt, there is an immediate outgrowth of black gold, which speedily changes to an advancing mass of yellow, or perhaps lilac metal in lichen-like forms, from which proceed beautiful fringes of yellow or black, ending generally in such arborescent forms as are represented in Fig. 7. As these branches

FIG. 7



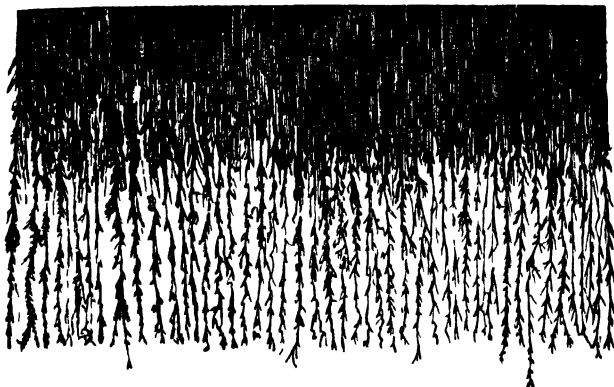
push into the yellow liquid, it becomes colourless even in advance of their points, and it frequently happens that yellow crystals of some salt shoot out in front of the crystallizing metal, which follows them

and builds up its advancing fronds at their expense. This is shown in the figure. The gold will generally shoot its yellow branches rapidly round the margin of the drop. Such a running branch has been seen to stop on touching at one point a loose piece of gold, which immediately in its turn became active, and commenced to sprout on its farther side.

Copper salts give round nodules, which have no crystalline appearance when deposited from moderately weak solutions, but a very strong solution of the chloride—about 40 per cent.—yields with zinc first a black thick growth, then arborescent fringes of red metal, terminating in crystals of very appreciable size.

The fringes referred to in the case of these three metals are still more characteristically developed by bismuth. When a solution of terchloride of bismuth acts on zinc there is an immediate outgrowth of black fringes, such as Fig. 8, where they are seen on an illuminated field. These as they advance become more and more arborescent, and as the crystalline character develops itself more they change from black to grey. Sometimes bismuth presents itself in botryoidal masses, but the tendency to form these fringes is very strong.

FIG. 8.



Chloride of antimony with zinc also gives these black fringes.

Lead salts yield crystals resembling those of silver; but leaves of irregular hexagonal plates prevail, and often grow to a large size.

A solution of acetate of thallium, containing 20 per cent. of salt, quickly gives a beautiful forest of thorny crystals.

Sulphate of cadmium gives rise to a small leaf-like growth on zinc; but a strong solution of the chloride produces an appearance of sticks covered with small spines or knobs.

The new metal indium is thrown down upon zinc in the form of thick white crystals. The deposition is promoted by touching the zinc with a piece of iron.

Tin gives beautiful results. If zinc be placed in a solution of stannous chloride it is quickly surrounded with an outgrowth of prolonged octohedra, and as these advance into the liquid it is easy to observe that the additions of new metal commence at the apex, and that the wave of chemical change proceeds down the lateral edge, occupying some seconds of time in depositing the new layer of material. Frequently, also, there is a luxuriant growth of large flat leaflets, or of symmetrical structures resembling fern-leaves, but with the fronds arranged at right angles, or combinations of these with octohedra, as shown in Fig. 6. These fern-leaves often begin of a dull grey colour; but, as they advance, suddenly change to a brilliant white.

The particular form of these crystalline growths depends, therefore, primarily, on the specific character of the metal; but this is greatly modified by the strength of the solution.

The forms assumed by native metals resemble those produced by this process of substitution. In some cases, indeed, it seems almost certain that the deposition of these minerals was effected in the same way, as, for instance, the silver which occurs sometimes in tufts, sometimes in large crystals, on the native copper of the Lake Superior district. Gold is frequently found in cubes more or less rolled, but the leaf gold from Transylvania bears a striking likeness to the crystals that form in our laboratory experiments. Silver is often found native as twisted hairs or wires of metal—a form that never occurs in the decomposition of its nitrate by copper, but which can be artificially produced in another way.

There has been noticed a singular tendency in old silver ornaments and coins to become crystalline and friable. Here is an ancient fibula from the island of Cyprus, supposed to be at least 1500 years old, which, through the greater portion of its substance, presents a fracture something like that of cast iron, and its specific gravity has been reduced in round numbers from 10 to 9. It contains a little copper. This property of certain metals, or their alloys, to change in condition and in volume, is worthy the attention of those whose duty it is to make our standards. Experiments should be instituted for the purpose of learning what metals or combinations of metals are least subject to this secular change.

These metallic crystals are Nature's first attempt at building. The material is the simplest possible—in fact, what chemists look upon as elementary. But how is the building carried on? What are the tools employed? Where are the bearers of burdens that bring the prepared pieces and lay them together according to the plan of the Great Architect? We must try to imagine what is taking place in the transparent solution. The silver, of course, existed at first in combination with the nitric element, and for every particle of silver deposited on the growing tree, an equivalent particle of copper is dissolved from the surface of the plate. The nitric element never ceases to be in combination with a metal, but is transferred from the

one metal to the other. On the "Polarization Theory," the positive and negative elements of the salt constantly change places and enter into fresh combinations, one consequence of which would be a gradual passage of the nitric element from the growing silver to the copper plate. This actually takes place, and there is a diminution of the salt at the ends of the silver branches, giving rise to an upward current, and a condensation of nitrate of copper against the copper plate, which gives rise to a strong downward current. These two currents are seen in every reaction of this nature. In the case of silver and copper, however, it has been proved that the crowding of the salt towards the copper plate is more rapid than would follow from the usual polarization theory. The instrument employed for determining this point was a divided cell in which two plates, one of silver and the other of copper, connected together by a wire, are immersed each in a solution of its own nitrate, contained in each division of the cell, and separated from one another merely by parchment paper. The crystals of silver deposited on the silver plate in this experiment are very brilliant.

There are other indications of the liquid being put into a special condition by the presence of the two metals which touch one another. Thus zinc alone is incapable of decomposing pure water; but if copper or platinum be deposited on the zinc in such a manner that the water can have free access to the junction of the two metals, a decomposition is effected; oxide of zinc is formed, and hydrogen gas is evolved. At the ordinary temperature the bubbles of gas rise slowly through the liquid, but if the whole be placed in a flask and heated, pure hydrogen is given off in large quantity. We have also found that iron or lead similarly brought into intimate union with a more electro-negative metal, and well washed, will decompose pure water.

As might be expected, the action of magnesium on water may be greatly enhanced by this method; and a pretty and instructive experiment may be made by placing a coil of magnesium in pure water at the ordinary temperature, when there will be scarcely any effect visible, and then adding a solution of sulphate of copper. The magnesium is instantly covered with a growth of the other metal, and at the same time the liquid seems to boil with the rapid evolution of hydrogen bubbles from the decomposed water.

When, however, the force of the two metals in contact has to traverse a layer of water, the resistance offered by the fluid prevents its decomposition. This must also be an important element in the decomposition of a metallic salt dissolved in water, and in fact we have found that the addition of some neutral salt, such as nitrate of potassium, increases the action—apparently by diminishing the resistance of the liquid. If, too, we increase the quantity of the dissolved metallic salt, we get more than a proportional increase of deposited metal. Thus, in an experiment made with the different strengths of nitrate of silver on the table, the following results were obtained in ten minutes, all the circumstances being the same except the strength

of the solution :—

1	per cent.	solution dissolved	·025	gram.	copper.
2	"	"	"	·078	"
4	"	"	"	·224	"

In fact it has been found that in solutions not exceeding 5 per cent., twice the amount of nitrate of silver dissolved in water gives three times the amount of chemical action; and this is true with other metals also in weak solution. It may be that this is not the precise expression of a physical law, but it agrees at least very closely with the results of experiment.

The power arising from this action of two metals on a binary liquid may be carried to a distance and produce similar decompositions there. This is ordinary electrolysis. Metals have often been crystallized from their solutions in this way, and Mr. Braham has made excellent preparations of crystalline silver, gold, copper, tin, platinum, &c., by using poles of the same metal as that intended to be deposited upon them. The forms thus obtained are precisely analogous to those produced by the simple immersion of one metal into the soluble salt of another, and illustrate still further the essential unity of the force that originates the two classes of phenomena.

[J. II. G.]

Friday, March 1, 1872.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

C. WILLIAM SIEMENS, D.C.L. F.R.S. M.R.I.

On Measuring Temperatures by Electricity.

THE truth revealed to us by one of the younger branches of physical science, which has been cultivated and expounded nowhere more effectually than within these walls, has divested heat and electricity of their mysterious character, and has taught us to regard them simply as "modes of motion."

Light also has been shown to be identical in its nature with heat, and the only remaining physical agency, "chemical affinity," has been recognized as a force differing only in "quality of action" from the others. According to these views, force, in whichever type of action it presents itself, is as *indestructible as matter itself*, and is therefore capable of being *stored up* and *measured* with the same certainty of result. We have a unit of force or the foot lb., and a unit of heat, or the heat necessary to raise the temperature of 1 lb. of water through one degree Fahr., and it has been already proved that 772 units of force are the equivalent value of one unit of heat. Again, the chemical force residing in 1 lb. of pure coal is equal to about 14,000 heat units, or $14,000 \times 772 = 10,808,000$ ft. lbs. = 4825 tons lifted one foot high.

Questions regarding the quantitative effects of heat present themselves, however, much less frequently for our consideration than questions regarding its *intensity*, upon which depends the nature of the phenomena surrounding us at every step, both in science and in ordinary life. The instrument at our command for determining moderate intensities or temperatures, the mercury thermometer, leaves little to be desired for ordinary use; but when we ascend in the scale of intensity, we soon approach a point when mercury boils, and from that point upward we are left without a reliable guide. The result is, that we find in scientific books on chemical processes, statements to the effect that such or such reaction takes place at a *dull red heat*, such another at a *bright red*, a *cherry red*, a *blood red*, or a *white heat*—expressions which remind one rather of the days of alchemy than of chemical science of the present day.

There are pyrometers, it is true, but these are either of a complex nature, or little reliance can be placed on them.

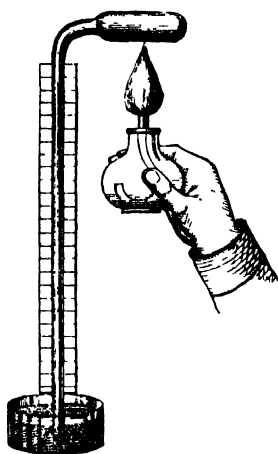
It is my purpose this evening to place before you an instrument

by which I hope to fill up to some extent the existing gap. It is the result of occasional experimental research, spread over several years, and it aims at the accomplishment of a double purpose, that of measuring high temperatures, and of measuring with accuracy the temperatures of *inaccessible* or *distant* places.

But before entering upon the details of my subject, I propose to place before you an instrument which fulfils, in principle, all the conditions essentially necessary in thermometry, and is at the same time the very first instrument that was ever proposed for measuring temperatures. I speak of the *air thermometer* by Galileo! It can be shown on theoretical grounds, that the expansion of a permanent gas at constant pressure is the most perfect index of temperature. It is in fact, the degree of energy of the atomical motion in an elastic fluid which determines its volume, and which constitutes at the same time its temperature.

The air thermometer consists simply of a bulb of glass with a long tubular stem, open to the atmosphere at its extremity. If I heat the bulb (by dipping it for instance into boiling water) and put it into a holder, with the hollow stem reaching downward into a cup of mercury, the air within the bulb will no longer communicate directly with the atmosphere, because the mercury is interposed. If now I cool the air within the bulb, by the external application of iced water its heat motion will diminish, and its volume would be reduced proportionally, if the external atmosphere could enter freely to fill up the vacancy thus created. But inasmuch as the external air cannot enter, a reduction of pressure will take place, which, according to the law of elasticity by Boyle, must be proportionate to the reduction of volume at constant pressure. The difference of pressure thus created between the bulb and the external atmosphere will be balanced by the column of mercury rising up into the tube, and the elevation to which the mercury attains is a true index of the temperature to which the air in the bulb had been previously heated. This is true with regard to all temperatures, from the lowest to the highest, and the instrument may be termed a universal thermometer. If the bulb could be cooled down to 273° Centigrade below the zero point, it would follow by the law of Charles that the elastic pressure of air would be reduced to nothing, that is to say, the motion of the particles of air, which we call heat, would have ceased, and we should

FIG. 1



have reached the point of absolute zero, a point which has been theoretically established also by other means.

Practically, such an instrument would be most inconvenient; its indications would have to be corrected by calculation for barometrical variations; the capacity of the descending tube, which contains air not subjected to variation of temperature, would have to be taken into account, and no reliable observations could be arrived at, without taking special precautions, such as are only within reach of the experimental physicist.

[The other known methods of measuring ordinary and furnace temperatures were here passed in review, and the limits of their application pointed out. They were classified into:

Thermometers, by expansion of liquids.

Thermometers, by the expansion of solids.

Pyrometers, by chemical decomposition of solids, comprising Wedgwood's and Deville's pyrometers.

Pyrometers, by observing the melting-point of metals.

Pyrometers, by thermo-electricity.

Pyrometers, by exposing a copper or platinum ball of known heat capacity to the heat to be ascertained, and of quenching it in a measured quantity of water.]

The instrument which forms the subject matter of my discourse presents many points of analogy with the air thermometer, if we substitute "*electrical resistance in conductors*" for "*expansion of gases*"! Both these effects are functions of temperature, increasing with the temperature according to progressive laws, which in the case of the gases we call the *law of Charles*, and in the case of conductors, the law of "*increase of electrical resistance with temperature.*" The latter law, which is of recent origin, had already been partially developed by Andsen, Swanberg, Lenz, and Werner Siemens, when my attention was directed, in 1860, towards an application of the same to the measurement of temperatures at places inaccessible to the ordinary thermometer. By means of the contrivance which I shall describe presently, I was enabled to tell, in the testing cabin of a cable ship, the increasing temperature of the interior of the mass cable in the hold, and to prove the necessity of transhipment of the same into a vessel fitted with water-tight tanks, which have been resorted to ever since, to avoid the danger of softening the gutta-percha covering.

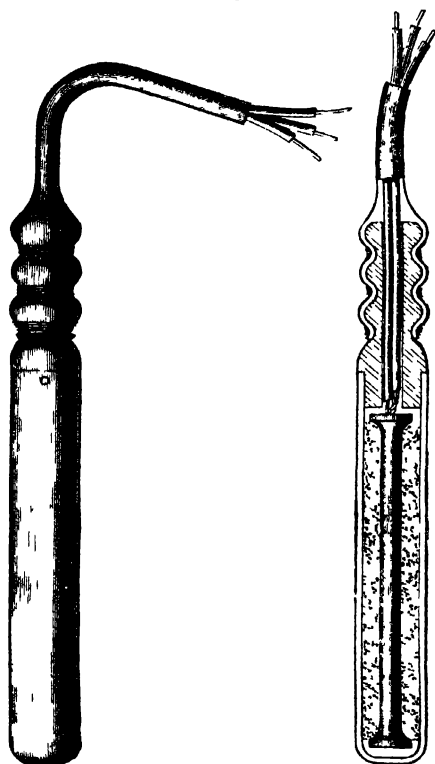
I have arranged an apparatus for proving to you in the first instance that the conductivity of a wire of platinum or other metal is greatly influenced by its temperature; for this purpose I direct the current of a galvanic battery at will through two branches of equal resistance, each branch comprising a free spiral wire of platinum and one of the coils of a differential galvanometer. By throwing the powerful light of an electric lamp upon the face of the differential galvanometer, and by throwing the image by means of a mirror and lens upon the screen, the audience will see any movement of the needle to the right or the left that may take place when I complete the battery connection. The

resistance of both branch circuits being the same, no deflection of the needle is observable on depressing the key, but when I pass the flame of a spirit-lamp under the one platinum coil the needle is thrown immediately over to the right, because the electrical resistance of the heated wire is increased, and consequently a larger proportion of the current is passing through the cooler circuit, exercising a preponderating influence upon the galvanic needle. When I withdraw the spirit flame from the wire the needle rapidly returns to its zero position, but in passing it under the other spiral wire the needle immediately deflects in the opposite direction.

If instead of using the open spirals I were to wind thin insulated wire of any pure metal upon two small cylindrical pieces of wood, and were to enclose the tiny spirals in small silver casings, as shown in *Fig. 2* and in section by *Fig. 2*, taking care that the extremities of the spiral wires were soldered to thicker insulated wires leading respectively to the battery and differential galvanometer before mentioned, it follows that no deflection of the needle ensues when both the protected and equal spirals are dropped into a jar containing iced water. But if I take one of the spirals from the water, and place it, for instance, by his kind permission, into the hand of our President without disconnecting the same from its leading wires, the balance of resistance will no longer take place, and a deflection of the needle to the right actually takes place.

I will now endeavour, however, to re-establish the equilibrium by adding warm water to the iced water surrounding the comparison coil near me until no deflection of the needle is observable. This result being obtained, it follows that the temperature of the water

FIG 2

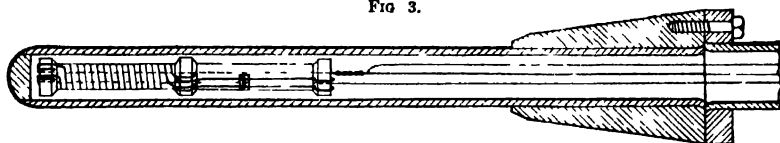


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surrounding the one coil must be identical with the temperature of our President's hand, and the delicate mercury thermometer which I have placed in my solution must give me the temperature of the distant place which I intended to measure. The temperature here observed is 89.5° Fahrenheit, which is at this moment that of Sir Henry Holland's hands. This result is independent of the ratio in which the electrical resistance increases with temperature in the similar coils, and considering that the silver casings containing the coils are not larger than small pencil-cases, this method might be advantageously employed in physiological research. The one coil would only have to be placed within the cavity to be measured to enable the observer to read the temperature from time to time, without disturbing the patient, with the accuracy of which the mercury or spirit of wine thermometer employed is capable. But the same method is applicable for measuring the temperatures of distant or inaccessible places, such as the interior of stores or cargoes of materials liable to spontaneous combustion; of points elevated above the surface of the ground; or of great depths below for meteorological purposes; or for measuring the temperature of the sea continuously in attaching such a coil to the mariner's sounding lead. An error would in such cases arise, however, through the uncertainty of the resistance of long leading wires, if a complete remedy of error from such a source had not suggested itself. This consists in uniting three separate insulated leading wires, into a cable by which the distant coil is connected with the measuring instrument. One galvanic circuit passes from the battery through one of the leading wires, through the distant spiral and back again through the second leading wire to the differential galvanometer and the battery, and the second passes from the same battery through the near coil, and through the third leading wire up to the distant coil without traversing the same, and back again through the second leading wire to the galvanometer and battery. Thus both galvanic circuits comprise the leading wires up to the distant coil, and all variations of resistance by temperature to which the leading wires may be subjected, affect both sides of the balance equally. In constructing coils for measuring deep-sea temperatures a large quantity of insulated copper or iron wire is wound upon a metallic tube open at both ends to admit the sea-water freely in order to impart its temperature to the innermost layers of the insulated wire. The coil of wire is protected externally by drawing a tube of vulcanized india-rubber over it, which in its turn is bound round by a close spiral layer of copper wire, whereby the sea-water is effectually excluded from the sensitive coil. By these arrangements the temperature of distant or otherwise inaccessible places can be accurately ascertained; but the method is limited to the range of temperature which can be obtained and measured in the comparison bath. In order to realize a pyrometer by electrical resistance, it is necessary to rely upon the absolute measurement of the electrical resistance of a coil of wire which must be made to resist intense heats without deteriorating

through fusion or oxidation. Platinum is the only suitable metal for such an application, but even platinum wire deteriorates if exposed to the direct action of the flame of a furnace, and requires an external protection. The platinum wire used has, moreover, to be insulated and supported by a material which is not fused or rendered conductive at intense heats, and the disturbing influence of leading wires had in this case also to be neutralized. These various conditions are very fully realized by the arrangement represented on the following diagram, Fig. 3.

FIG 3.



Thin platinum wire is coiled upon a cylinder of hard-baked porcelain, upon the surface of which a double-threaded helical groove is formed for its reception, so as to prevent contact between the coils of wire. The porcelain cylinder is pierced twice longitudinally for the passage of two thick platinum leading wires, which are connected to the thin spiral wire at the end. In the upper portion of the porcelain cylinder the two spiral wires are formed into a longitudinal loop, and are connected crossways by means of a platinum binding screw, which admits of being moved up or down for the purpose of adjustment of the electrical resistance at the zero of Centigrade scale. The porcelain cylinder is provided with projecting rims, which separate the spiral wire from the surrounding protecting tube of platinum, which is joined to a longer tube of wrought iron, serving the purpose of a handle for moving the instrument. If the temperatures to be measured do not exceed a moderate white heat, or say 1300° Centigrade = 2372° Fahr., it suffices to make the lower protecting tube also of wrought iron, to save expense. This lower portion only, up to the conical enlargement or boss of iron, is exposed to the heat to be measured. Three leading wires of insulated copper united into a light cable connect the pyrometer with the measuring instrument, which may be at a distance of some hundred yards from the same. They are connected by means of binding screws at the end of the tube to three thick platinum wires passing down the tube to the spiral of thin platinum wire. Here two of the leading wires are united, whereas the third traverses the spiral, and joins itself likewise to one of the two former, which forms the return wire for two electrical circuits, the one comprising the spiral of thin wire, and the other returning immediately in front of the same, but traversing in its stead a comparison coil of constant resistance. The measuring instrument may consist of a differential galvanometer as before, if to the constant resistance a variable resistance is added. If the pyrometer coil were to be put

into a vessel containing snow and water, the balance of resistance between the two battery circuits would be obtained without adding variable resistance to the coil of constant resistance, and the needle of the differential galvanometer would remain at zero when the current is established. But on exposing the pyrometer to an elevated temperature the resistance of its platinum coil would be increased, and resistance to the same amount would have to be added to the constant resistance of the measuring instrument, in order to re-establish the electrical balance. This additional resistance would be the measure of the increase of temperature, if only the ratio in which platinum wire increases in electrical resistance with temperature is once for all established. This is a question which I shall revert to after having completed the description of the pyrometric instrument.

Although I have explained that by means of a differential galvanometer and a variable resistance (constituting in effect a Wheatstone bridge arrangement) the increasing resistance of the platinum spiral may be measured, it was found that the use of a delicate galvanometer is attended with considerable practical difficulty in iron-works and other rough places where it is important to measure elevated temperatures, or on board ship for measuring deep-sea temperatures. I was therefore induced to seek the same result by the conception of an instrument which is independent in its action from tremulous motion, or from magnetic disturbance caused by moving masses of iron, and which requires no careful adjustment or special skill on the part of the operator. This instrument is represented by Fig. 4 on page 446, and may be termed a chemical resistance measurer or "differential voltameter." The immortal Faraday has proved that the decomposition of water in a voltameter expressed by the volumes of gases V , is proportionate in the unit of time to the intensity I of the decomposing current, or that .

$$I = \frac{V}{T}.$$

According to Ohm's general law, the intensity I is governed by the electro-motive force E , and inversely by the resistance R , or it is

$$I = \frac{E}{R}.$$

It is therefore

$$\frac{V}{T} = \frac{E}{R} \text{ or } V = \frac{E T}{R};$$

or the volume V would give a correct measure of the electrical resistance R if only the electro-motive force E and time T were known and constant quantities. But the electro-motive force of a battery is very variable; it is influenced by polarization of the electrodes, by temperature, and the strength and purity of the acid employed. The volume of gases obtained is influenced, moreover, by the atmospheric

pressure, and it is extremely difficult to make time observations correctly. It occurred to me, however, that these uncertain elements might be entirely eliminated in combining two similar voltmeters in such a manner that the current of the same battery was divided between the two, the one branch comprising the unknown resistance to be measured, and the other a known and constant resistance. The volume of gas V' produced in this second voltmeter, having a resistance R' in circuit, would be expressed by

$$V' = \frac{E T}{R'}$$

and we should have the proportion of

$$V : V' = \frac{E T}{R} : \frac{E T}{R'} ;$$

or E and T , being the same in both cases, may be struck out, and the expression will assume the simple form

$$V : V' = R' : R.$$

The constant resistance R of the one circuit being known, it follows that the unknown resistance R' is expressed, by $\frac{R V'}{V}$; that is to say, by a constant multiplied by the proportion of gas produced in the two voltmeters irrespective of time, or strength of battery, or temperature, or the state of the barometer.

The resistance R and R' are composed each of two resistances, namely, that of the principal coils, which we may term R or R' , and of the voltmeter and leading wires, which is the same in both cases, and may be expressed by y . The expression should therefore be written as follows:

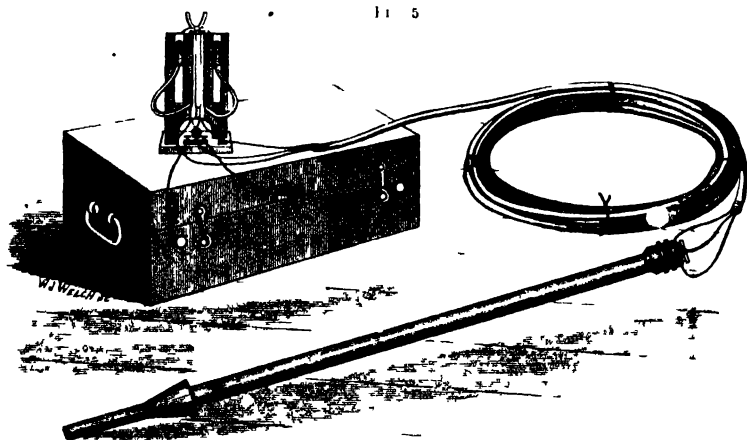
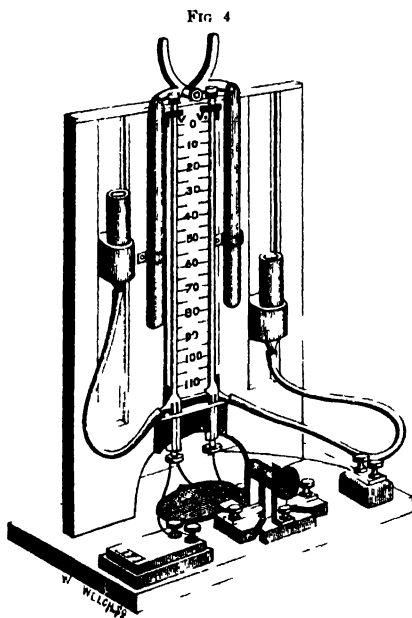
$$V : V' = R' + y' : R + y,$$

R' being the unknown quantity.

The mechanical arrangement of the instrument will be understood from the diagram, Fig. 4; and the whole arrangement of the pyrometer, with its leading wire and resistance measurer, from the general view given in Fig. 5. The voltametric resistance measurer consists of two calibrated vertical tubes of glass of about 3 millimètres diameter, which are fixed upon a scale showing arbitrary but equal divisions. The upper ends of the tubes are closed by small cushions of india-rubber pressed down upon the openings by means of weighted levers, whereas the lower portions of the tubes are widened out and closed by plugs of wood, through which the electrodes in the form of pointed platinum wires penetrate to the depth of about 25 millimètres into the widened portions of the tubes. By a side branch the widened portion of each vertical tube communicates by means of an india-rubber connecting pipe to a little glass reservoir containing acidulated water, and supported in a vertical slide. In raising the weighted cushions closing

the upper ends of the vertical tubes, and in adjusting the position of the small reservoirs, the acidulated water will rise in both tubes to the

zero line of the scale. In turning a button in front of the tubes the battery current is passed through both pairs of electrodes, the one circuit comprising the permanent resistance R and the leading wires up to the pyrometer, and the other the leading wires and the pyrometer coil. If the resistance of the pyrometer coil should be equal to the permanent resistance R , the $R' + y$ will be equal to $R + y$, and therefore $V = V'$, but as the resistances differ, so will the volumes. Necessary conditions are: that both reservoirs are filled with the same standard solution of pure water with about 10 per cent. of sulphuric acid, that all the electrodes are of the same form and size, and that their polarity is reversed frequently during the progress



of each observation, in order to avoid unequal polarization. With these precautions, which involve no particular skill or knowledge of elec-

trical observation on the part of the operator, very accurate results are obtained; but in order not to incur considerable error of observation it is advisable to continue the current, reversing the same say twice, until at least forty divisions of gases are produced in the least activated tube, which operation will occupy from 2 to 3 minutes; if a battery, of from 4 to 6 Daniell elements is employed. The volumes V and V' being noted, after having allowed half a minute for the gases to collect after the current has ceased, the weighted cushions upon the tubes are raised in order to allow the gases to escape, when the water levels will immediately return to their zero position, to make ready for another observation. By inserting the observed values for V and V' into the expression above given, the unknown resistance R' can be easily calculated; but in order to facilitate the use of the instrument I have prepared a Table which gives at a glance the resistance due to any two observed volumes, the volumes V governing the vertical, V' the horizontal column, and the resistance being read off at the point of intersection. At each point of intersection the resistance is marked in black, and the corresponding temperature in red ink.

It now remains only to be shown what is the relation between the resistance and temperature in heating a platinum wire. The researches of Dr. Matthiessen, who has made the latest investigations on the effect of temperature upon electrical resistance, are restricted to the narrow range of temperatures between 0° and 100° Centigrade, nor do they comprise platinum. He adopted the following general expression for the pure metals:

$$R_t = \frac{R_0}{1 + \alpha t + \gamma t^2},$$

which, in determining the specific values of α and γ for each metal, gives a close agreement with observation between the narrow limits indicated, but is wholly inapplicable for temperatures exceeding 200° Centigrade, when the value t^2 commences to predominate and to produce absurd values for R_t .

It was necessary for my purpose to undertake a series of elaborate experiments with a view of finding a ratio of general application. Coils of thin wire, of platinum, iron, copper, and some other metals, were gradually heated and cooled in metallic chambers containing the bulbs of mercury thermometers, and for higher temperatures of air thermometers, and the electrical resistances were carefully noted. The progressive increase of electrical resistance was thus compared directly with the increasing volume of a permanent gas (carefully dried) between the limits of zero and 470° Centigrade and a ratio established, which is represented by the formula

$$R_t = \alpha T + \beta T + \gamma,$$

in which T signifies total temperature counting from the absolute zero, and α , β and γ specific coefficients for each metal. According to this formula the electrical resistance is a constant at the absolute zero, and

progresses in a ratio represented graphically by a tipped-up parabola, approaching more and more toward a uniform ratio at elevated temperatures. Although the comparison with the air thermometer could only be carried up to 470° Centigrade, the general correctness of the ratio of increase just stated has been verified by indirect means in measuring progressive heats, and by comparison with the platinum ball pyrometer.

It is important to mention here that great care must be exercised in the selection of the platinum wire for the measuring spiral, platinum wire having been met with conducting only 4.7 times better than mercury at zero, Centigrade, and others, conducting 8.2 times better than mercury, although both samples had been supplied by the same eminent makers, Messrs Johnson and Mathey. The abnormal electrical resistance of some platinum wire is due chiefly to the admixture of iridium or other metals of the same group, and it appears that the platinum prepared by the old welding process is purer and therefore better suited for electrical purposes than the metal consolidated by fusion in a Deville furnace.

In conclusion, I shall show some working results of the pyrometer in measuring by means of the same protected coil a mixture of ice and water, boiling water, molten lead, and the fire itself by which the lead is melted, the readings produced being 2° Centigrade, 98° Centigrade, 330° Centigrade, and 860° Centigrade respectively. The latter temperature signified a cherry red heat, as may be judged by the appearance of the tube when withdrawn from the fire. The instrument which I have had the honour to bring before you this evening has already received several useful applications. Through its first application an important telegraph cable was saved from destruction through spontaneous generation of heat. Prof. Bolzani, of Kasan, has made some interesting applications of it for recording the temperature at elevated points and at points below the earth's surface. Mr Lowthian Bell has used it in his well-known researches on blast-furnace economy, and at several iron-works pyrometer tubes are introduced into the heating stoves, and permanently connected with the office, where the heat of each stove can at all times be read off and recorded. These and other applications are sufficiently self-evident, if the soundness of the principles upon which I rely is conceded, but I feel that the shortness of time at my command has hardly enabled me to do more than to pass these in review, while endeavouring to demonstrate the results obtained of recording the temperatures of distant or inaccessible places, including furnace temperatures.

[C. W. S.]

April 19, 1872.

SIR FREDERICK POLLOCK, Bait. M.A. Vice-President, in the Chair.

A. VERNON HARCOURT, Esq. F.R.S. Sec. Chem. Soc.

On the Sulphurous Impurity in Coal Gas.

THE luminous flames we use to light our houses after sunset are all equally gas flames.

The gas which burns round the wick of a candle is formed by the action of heat on the grease of which the candle is made. The gas which burns over the wick of an oil lamp is formed by the action of heat on the oil. The gas which burns over a "gas-burner" is formed by the action of heat on coal.

By the heating of any of these substances many different kinds of gas are produced, some of which become liquids if they are allowed to cool, while others are permanently gaseous. In the case of candles and lamps, when the hot gas is burnt as fast as it is made, the undensable and the condensable are burnt alike, the latter contributing even more than the former to the luminosity of the flame. In the case of coal gas, which is kept for many hours, and has often to travel along many miles of iron piping before it is burnt, only very little condensable gas reaches the burner. In this respect "gas" illumination is at a great disadvantage as compared with candles or lamps. To counter-balance this disadvantage gas must be produced from some substance which is much cheaper than grease or oil, and such a substance we have in coal. But coal, like all minerals obtained on the large scale, is mixed with small quantities of other substances, and, in particular, masses of coal always contain a greater or less proportion of a mineral known, according to its form, as pyrites or marcasite, composed of eight parts of sulphur united with seven of iron. When coal is heated, a part of the sulphur from this mineral unites with the carbon and hydrogen of the coal, and thus the illuminating gas formed from coal is contaminated with at least two sulphur compounds—carbon bisulphide and hydrogen sulphide. Such gas yields when it is burnt, in addition to water and carbon dioxide, sulphur dioxide produced by the burning of the sulphur. This gas has a well-known pungent smell; it acts on various colouring matters, and it is gradually changed in presence of air and moisture into a far more destructive substance called hydrogen sulphate or oil of vitriol. Unlike sulphur dioxide, which is a gas and can be removed by ventilation, hydrogen sulphate

is not volatile, and exerts a continued corrosive action upon organic materials or fabrics on which it is deposited. In a furnished room the leather bindings of books and coverings of furniture are especially liable to be injured thus; perhaps because this material, being a better conductor of heat than others which are used for the same purposes, is more bedewed after gas has been lighted in a room than they are, and also because it requires less often to be cleaned or renewed. Fortunately the conversion of sulphur dioxide into hydrogen sulphate takes place so slowly that in a room lighted with gas and well ventilated a very small part of the sulphur which gas is liable to contain remains in this destructive form. Fortunately, also, the quantity of sulphur which gas as at present manufactured is liable to contain is very small. In a room lighted with four gas-burners the volume of sulphur dioxide mixed with the atmosphere of the room in the course of an hour is about one-hundredth of a cubic foot. The amount actually present at any moment, if the room is fairly ventilated, is a small fraction of this volume. Nevertheless, it is possible, and even probable, that some injury, especially to the bindings of books, may in the course of years be caused under these circumstances; and it is desirable, with a view to avoiding any such injury, and also with a view to allaying the apprehension of it, that the proportion of sulphur compounds in coal gas should be reduced as far as possible.

A ton of coal may contain about 30 lbs. of sulphur: it yields nearly 10,000 cubic feet of gas, and a considerable part of the sulphur contained in it is given off with the gas in combination with either carbon or hydrogen. Of these two elements, hydrogen claims by far the larger proportion, not less than ten parts for one that is united with carbon. For the purification of gas from hydrogen sulphide excellent methods are everywhere in use. The gas is passed through layers of slaked lime or of iron oxide, by either of which substances all the hydrogen sulphide is capable of being completely absorbed. But the smaller quantity of sulphur existing in the form of carbon bisulphide is not arrested by these agents, nor is there at present any material or process known by which it can be effectually removed.

When coal gas which is pure from hydrogen sulphide is heated and tested again, it is found to contain this impurity, showing that some ingredients of the gas are capable of producing hydrogen sulphide by their mutual action. Hydrogen seems to have a much stronger affinity for sulphur than carbon has. One consequence of this difference is the unequal partition of the sulphur between the two elements in the gas retort. But this inequality does not reach its limit in the short time which elapses between the formation and cooling down of the gas; and accordingly, when foul gas (or gas which has not been purified from hydrogen sulphide) is further heated, the proportion of hydrogen sulphide in it is increased, and that of carbon bisulphide diminished. From a number of experiments in which foul gas was passed through an iron tube three inches in diameter, filled with iron turnings and heated for a length of about

two feet to low redness, it appeared that the amount of carbon bisulphide could be so far reduced that the gas, after purification from hydrogen sulphide, contained five or six instead of thirty grains of sulphur in 100 cubic feet. The gas was driven through the heated tube at a rate of from one to two cubic feet a minute.

A somewhat greater reduction in the amount of sulphur is obtained by heating the gas after, instead of before, purification and purifying it a second time. If it is the case, as seems probable, that the sulphur present in coal gas distributes itself when the gas is heated between the carbon and hydrogen in a ratio dependent upon the relative affinity for sulphur of the two elements, the proportion of carbon bisulphide to the total sulphur in the gas will be always the same when the composition of the gas is the same, and when it has been heated long enough for the establishment of an equilibrium. Accordingly we should expect the removal of sulphur, by the conversion of carbon bisulphide into hydrogen sulphide and the absorption of the latter, to be accomplished more effectually with gas from which the chief part of the sulphur had already been extracted. And this, as has already been stated, is found to be the case.

The nature of the chemical change which takes place when coal gas is heated may be illustrated by passing hydrogen over the mouth of a tube containing carbon bisulphide, and thence through a piece of combustion tubing heated nearly to a red heat. The mixture of hydrogen and carbon bisulphide vapour has no action on a solution of lead acetate; but, after the application of heat, the gas which issues produces at once a black precipitate, proving that hydrogen sulphide has been formed. This change occurs readily with hydrogen which has been carefully dried; but the presence of moisture appears to promote it; and as coal gas contains a quantity of aqueous vapour, much more than sufficient to react with the maximum amount of carbon bisulphide, it is possible that the formation of hydrogen sulphide when coal gas is heated, may be partly due to the intervention of moisture.

If clean iron nails are heated to redness in a glass tube, and coal gas is passed slowly over them, a soft black carbonaceous deposit is formed, and the gas is deprived of a part of its carbon. If, however, the gas be passed through more rapidly, no such deposition takes place, although the time of contact of the gas with the heated surface is still sufficient to effect the conversion of the carbon bisulphide into hydrogen sulphide. In the latter case it may be presumed that no change occurs in the illuminating power of the gas. But to establish a point which is of capital importance, some direct observations were made on the illuminating power of gas thus treated. It was found with gas passing at the rate of 5 cubic feet an hour through a half-inch iron tube, heated for a length of 12 inches, that, when the heat did not exceed low redness, no change was observable. When the heat was raised to bright redness, there was a perceptible increase in the illuminating power.

If the process of heating coal gas, in order to remove the sulphur contained in it, should be employed on the manufacturing scale, the rate of transmission of the gas through the heating apparatus would necessarily be such as to render any deposition of carbon very unlikely. But even where such deposition takes place, it is not necessarily accompanied by a diminution of the illuminating power.

An interesting experiment, from this point of view, is the decomposition of marsh gas by the electric spark. When a stream of sparks from a Ruhmkorff coil is transmitted between the ends of platinum wires through a small quantity of marsh gas enclosed in a glass tube over mercury, the gas gradually expands. In about ten minutes it is nearly doubled, and at the same time a black deposit appears on the tube, in the neighbourhood of the wires. Here the intense heat applied has effected an almost complete decomposition of the hydrocarbon into its elements. But at the same time there is found a small quantity of some more condensed hydrocarbon, probably acetylene. On expelling the gas through a jet attached to the upper end of the tube, and burning it, the flame is seen to be much more luminous than that of marsh gas itself. The fact of which this experiment gives a striking illustration is that the illuminating power of gas depends much more upon the nature of the hydrocarbons it contains, than upon the total amount of carbon. How great would be the gain to the manufacturers of coal gas, if such an operation as this were possible on the large scale, by which the volume of gas is doubled and its illuminating power, at the same time, greatly increased!

As far as chemistry is concerned, the simple operation of heating gas appears to offer the means of a sufficiently perfect purification. The construction of a suitable system of iron pipes for heating the gas, and the best mode of obtaining and applying heat, is a problem for the engineer. On the scale on which gas is manufactured, all the apparatus for dealing with it must be of a magnitude to which it is difficult to pass, even in imagination, from the small scale of laboratory experiments; but, otherwise, the problem does not appear to be one of any peculiar difficulty. It may perhaps be found possible to employ some of the waste heat of the retort-house for this purpose, and thus to effect the required purification without much increasing the consumption of fuel.

[A. V. H.]

Friday, May 3, 1872.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM SPOTTISWOODE, Esq. LL.D. M.A. Treasurer R.S. and R.I.

On Optical Phenomena produced by Crystals submitted to Circularly Polarized Light.

ON a former occasion I exhibited some phenomena depending upon circular, or, as it was then also called, successive, polarization, and in particular I adopted and explained a method for producing circularly polarized light devised by Sir Charles Wheatstone. I propose on the present occasion to pursue the subject into some of its ulterior consequences. In terms of the wave theory, light is said to be circularly polarized when the vibrations are circular, as distinguished from plane polarization, when they are rectilinear. And further, it is known from mechanical principles that a circular vibration may always be produced by the combination of two rectilinear vibrations, the amplitudes or extents of which are equal, and whereof one is in advance or in rear of the other by one or by any odd number of quarter-wave lengths. In the former of these cases the circular motion will take place in one direction, say right-handed; in the latter in the opposite, say left-handed. The contrivance used for producing circular polarization this evening is known by the name of a "quarter-undulation plate," and consists of a plate of mica split to such a thickness that one of the two rays into which plane polarized light is divided on entering it is retarded by an odd number of quarter-wave lengths behind the other.

The optical phenomena produced by crystals when submitted to polarized light are usually divided into two classes, viz. (1) those arising from the use of parallel light, and consisting of broad sheets of colour; and (2) those due to convergent light, and consisting of the rings and brushes, the general character of which is well known. I propose to take a few specimens from each class, and to examine the modifications which the known phenomena undergo when the light is both polarized and analyzed circularly, i.e. when one quarter-undulation plate is interposed between the polarizer (Nicol's prism) and the crystal to be examined, and the second between the crystal and the analyzer (Nicol's prism).

In the first place, it is known that if a plate of selenite be placed in an ordinary apparatus when the polarizer and analyzer are either parallel or crossed, there are four positions at 90° apart in which the plate will produce colour; and further, that if the analyzer be turned through 90° the same result will be obtained, except that the colour will be complementary to that first seen. The intensity of the light at any given point is then given by the formula:

$$\cos.^2 s - \sin. 2i \sin. 2(i - s) \sin.^2 \frac{\theta}{2},$$

where i and s are the angles made with the original plane of polarization by the principal sections of the crystal and of the analyzer respectively, and θ is the retardation.

If, however, the two quarter-undulation plates (say the plates A and B) be introduced, the light undergoes the following processes:—First, it is plane polarized by the polarizer; secondly, the plate A being placed so that its axis is inclined at $\pm 45^\circ$ to the original plane of polarization, the light undergoes right or left handed circular polarization, and in that condition falls upon the crystal; thirdly, in their passage through the crystal C the rays are each divided into two, whose vibrations are at right angles to one another, and whereof one is retarded in proportion to the thickness of C; fourthly, the plate B being placed so that its axis is parallel or perpendicular to that of A, each of these sets of rays is circularly polarized, one set right-handed and the other left-handed; fifthly, these two oppositely circularly polarized sets of rays combine, according to known mechanical laws, on emerging from B into plane rays, in which the planes of polarization of the different colours of the spectrum are turned through different angles. Hence finally by turning the analyzer round we shall cross these various planes in turn and successively extinguish the different colours, leaving the complementary colours visible. The system of plates A C B consequently acts in this respect like quartz. It is, however, to be observed that if the plate B be turned from one of the two proposed positions to the other, the directions of motion in the two emergent circularly polarized rays, and consequently the planes of polarization of the different colours, will be reversed; in other words, with the plate B in one position we shall imitate a right-handed, with the plate B in the other a left-handed, quartz. The intensity of the light at any point is then given by the formula:

$$\sin.^2 \frac{\theta}{2} \text{ for one position,}$$

$$\cos.^2 \frac{\theta}{2} \text{ for the other.}$$

Again if, the plates A B retaining either of the positions before indicated, the crystal C be turned round in its own plane; then, since the light emerging from A and B is circularly polarized, it has lost

all trace of direction with reference to the positions of the polarizer and analyzer, and consequently no change of tint will be observed. The same is abundantly clear from the formula written above, because the only term it contains depends upon the retardation within the crystal C. This experiment was made by Airy.

If the plates A and B have their axes directed 45° on either side of the axis of C, and the three plates be turned round as one piece, the colour will remain unchanged; while, if the analyzer be turned, we have the colours shown in the regular order. If the plates A and B have their axes directed at 45° on the same side of the axis of C, and the pieces be turned round bodily as before the colours change in the same order as above, and go through their cycle once in every 90° of rotation; and if the analyzer be turned in the same direction, the colours change, but in the reverse order. The explanation of this is to be found in the fact that when the plates A and B are crossed, the retardation due by A is compensated by that due to B; so that the only effective retardation is that due to the crystal C. But upon this depends the rotation of the plane of polarization; if therefore the polarizer and analyzer remain fixed, the colour will remain unaltered. When the plates A and B have their axes parallel, there is no compensation, and the colour will consequently change. This experiment was made by Fresnel. The mathematical expressions for the intensity of the light in the two cases respectively are:

$$\cos^2 \left(j + i + \frac{\theta}{2} \right), \text{ and } \cos^2 \left(j - i - \frac{\theta}{2} \right),$$

where i is the angle made by the principal sections of A with that of the polarizer, and j that of the principal section of B with that of the analyzer. The first expression is obviously unchanged when the angle between the polarizer and analyzer, *viz.* $\frac{\pi}{2} + i + j$, is unchanged.

It should be added that the rotation of the plane of polarization, and consequently also the sequence of tints, does not follow exactly the same law in the above cases as in quartz.

We now come to the case of convergent light, that is, to the phenomena of crystal rings. And let us examine the effects produced by the same arrangement as before, *viz.* two quarter-undulation plates A, B, one in front and one behind the crystal C. To quote from Mr. Airy:—"The first thing that strikes us in this combination is that there is nothing, except in the crystal, that has any respect to sides. For the only incident light is circularly polarized; the only light allowed to emerge is circularly polarized. The appearance therefore of the coloured rings, &c., must be such as conveys no trace of any plane of polarization, and must not vary as the crystal is turned round. In the common exhibition of the coloured rings the principal trace of the planes of polarization is in the uncoloured brushes. In uniaxial crystals they form an eight-rayed star, composed of two

square crosses, inclined at an angle equal to that between the planes of polarization, every ray of which separates complementary rings. In biaxial crystals they compose two pairs of rectangular hyperbolas, the angle between whose asymptotes is the same as that between the planes of polarization, and whose branches divide complementary rings. The two crosses or two sets of hyperbolas unite when the planes of polarization are parallel or perpendicular. But in the case under consideration the rings exhibited by crystals will not be traversed by any brushes. Uniaxial crystals will exhibit circular rings without a cross; and biaxial crystals will exhibit complete lemniscates, without any interruption from curved brushes." And it is further to be noticed, as the formula given above indicates, that the centres of the rings will be bright or dark according as the analyzer stands at 0° or 90° .

To pursue this matter further. Suppose that, the arrangements remaining otherwise as before, the analyzer be turned round; then in any position intermediate to 0° and 90° the rings will be contracted and extended in opposite quadrants until at 45° they are divided by two diagonals, on each side of which the colours are complementary. Beyond 45° the rings begin to coalesce until at 90° the four quadrants coincide again. During this movement the centre has changed from bright to dark. If the motion of the analyzer be reversed, the quadrants which before contracted now expand, and *vice versa*. Again, if the crystal (say positive) be replaced by another (say negative), the effect on the quadrants of the rings will be reversed. This method of examination therefore affords a test of the character, positive or negative, of a crystal.

A similar process applies to biaxial crystals; but in this case the diagonals interrupting the rings are replaced by a pair of rectangular hyperbolas, on either side of which the rings expand or contract, and the effect is reversed either by reversing the motion of the analyzer, or by replacing a positive by a negative crystal, or *vice versa*. The experiment may then be made in biaxial crystals by turning the analyzer slightly to the right or to the left, and observing whether the rings advance towards, or recede from, one another in the centre of the field. In particular, if polarizer and analyzer being parallel, the plate A have its axis in a N.E. direction to a person looking through the analyzer, the plate B its axis in a N.W. direction, and the crystal be so placed that the line joining the optic axes be N.S., then on turning the analyzer to the right the rings will advance to one another if the crystal be negative, and recede if it be positive. The mathematical expression for the intensity of the light at any point P is in this case

$$\frac{1}{2} (1 + \sin. 2j \cos. \theta + \sin. 2b \cos. 2j \sin. \theta),$$

where b is the angle between the principal section of C through P and the principal section of B, and j the angle between the principal sections of B and the analyzer. This shows that when the polarizer and analyzer are parallel or crossed at 0° or 90° , and consequently $j = 45^\circ$

or 135° the expression is independent of b , i.e. the intensity is the same throughout circles about the centre, but that when the polarizer and analyzer are crossed we have an expression of the form

$$\frac{1}{2} (1 \pm \sin. 2 b \sin. \theta),$$

the sign of the second term depending upon the direction in which the analyzer has been turned, and also upon the sign of θ , that is, upon the character (positive or negative) of the crystal.

The dispersion of the planes of polarization effected by the passage of plane polarized light through a plate of quartz cut perpendicular to the axis may be rendered visible by interposing such a plate of quartz between the polarizer and a uniaxial or biaxial crystal, when the analyzer is at 90° , i.e. when dark brushes are formed. In this case the brushes cease to be black and are tinged throughout with colour. The analyzer must, however, be turned back or forward, according as the quartz be right-handed or left-handed, in order that it may cross in succession the planes of polarization of the different coloured rays, and so produce the most vivid effects. The dispersion of the brushes by a plate of quartz may however be studied by employing an additional polarizer and quartz plate between the source of light and the whole system previously used. By turning this polarizer round we extinguish each ray of the spectrum in turn and tint the whole field with the complementary colour. The brushes will then appear to revolve about their centres as the tints vary continuously from one end of the spectrum to the other. If the polarizer be turned still farther round, the tints which had changed continuously from red to violet, or *vice versâ*, change suddenly from violet to red, or *vice versâ*, and the brushes jump suddenly back to their original position.

This last optical arrangement may be employed to examine the more important phenomena of the dispersion of the optic axes produced, not by a quartz plate between the usual polarizer and crystal, but by certain biaxial crystals themselves.

[W. S.]

Friday, June 7, 1872.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

PROFESSOR ODLING, F.R.S.

On the History of Ozone.

THE most important points in the history of ozone are the following : I. Its recognition as a distinct variety of matter or substance, by Schönbein in 1840. II. An inquiry into its nature, made by Marignac in 1845, whereby it was established that the action of ozone on various substances results simply in their oxidation. III. The evidence of different kinds, accumulated by many observers during a period extending from 1845 to 1863, that the matter of ozone is identical with the matter of oxygen. IV. The demonstration by Andrews and Tait in 1860, that ozone is a condensed form of oxygen. V. The recognition by Andrews and Tait in 1860, and interpretation by the speaker in 1861, of the singular fact that, in certain cases, the removal of its constituent ozone from a mixture of ozone and oxygen is unattended by any alteration in the volume of the gas, notwithstanding the considerable oxidation effected by it. VI. The study of the quantitative reactions of ozone by Brodie in 1872; and his establishment of the relationship of ozone to ordinary oxygen, in corroboration of some less exact results obtained by Soret in 1865, as also of a suggestion made by the speaker in 1861.

I.

Ozone was discovered by Schönbein, in 1840, when experimenting with the then newly-invented battery of Sir Wm. Grove,—an instrument still recognized as yielding a current superior, in respect of joint quantity and intensity, to the current yielded by any other electro-motor available for general use. Ozone was recognized by Schönbein successively, as a minute constituent of the oxygen gas resulting from the electrolysis of water effected by a current of high tension; as a minute constituent of air or oxygen through which electric discharges have taken place; and as a minute constituent of air in which moist phosphorus has been undergoing slow oxidation. To Schönbein then is due the great merit of recognizing ozone as a distinct form of matter, having an identity of its own by whatsoever means prepared—

as also the merit of discovering the most important means for the production of ozone, and of establishing its principal properties and reactions.

The general properties of ozone are those of an active oxygenant. Thus, like chlorine and peroxide of nitrogen, it bleaches colouring matters, corrodes fabrics, tarnishes or otherwise attacks metals, and liberates iodine from iodide of potassium. Its special properties are its characteristic pungent odour, its destructibility by a moderate heat, and its non-manifestation of any acidulous reaction.

II.

The nature of ozone was at first the subject of much speculation, Schönbein inclining to the view that it was a new elementary body, and a component of nitrogen. But in 1845, Marignac, in a series of most exact experiments, made partly in association with De la Rive, brought the question as to the nature of ozone within a very narrow compass. The experiments of these investigators, in which they established, among other points, that by exposure to the action of ozone, moist silver was converted simply into oxide of silver, and iodide of potassium into its oxidized form of iodate of potash, were susceptible only of one or other of two interpretations—either the interpretation which they themselves put on their results, that the matter of ozone is identical with the matter of oxygen—or, else the interpretation put on their results by Schönbein, that ozone is constituted of oxygen plus the elements of water, or in other words, that it is a peroxide of hydrogen. For a long time, experiment seemed quite incompetent to decide between these two views—opposite conclusions being arrived at almost alternately by the different investigators engaged on the inquiry. Corroboration, however, if any were needed, of the fact that ozone is really formed from oxygen itself with or without water, and not from any trace of nitrogen or other foreign matter that might possibly be present, was afforded by a remarkable experiment conducted by Fremy and Becquerel in 1853, being, indeed, the first recorded quantitative experiment made with ozone. By passing a long series of electric discharges through a given volume of oxygen standing over an aqueous solution of iodide of potassium, Messrs. Fremy and Becquerel succeeded in causing the whole of this oxygen to assume the form of ozone; as was shown by its ultimate complete absorption by the solution, with correlative liberation of iodine from the dissolved iodide of potassium.

The difficulty experienced in those early days of making out the real nature of ozone—of ascertaining whether it is a form of oxygen or a peroxide of hydrogen—depended mainly on the very small degree to which it was then possible to charge air or oxygen with the ozone to be examined, and on the necessity for the exclusive employment in the investigation of apparatus in which neither metal nor organic matter was present for the ozone to react with. The apparatus had

consequently to be constructed entirely of glass, and all the junctions to be made before the blow-pipe or by grinding. Now-a-days, by improvements in the methods of conducting the processes of electrization and electrolysis, it is possible to charge oxygen with ozone in very considerable proportion; while by means of paraffin, a substance on which ozone is without recognizable action, junctions of the glass apparatus employed may be made and unmade with the greatest facility.

III.

Assuming the ozone furnished by the three principal processes for its production to be one and the same substance, it was not until the year 1863 that the absolute freedom of ozone from any proportion of hydrogen was so definitely established as not to allow of any further question. In this year, Soret showed that although ozonized oxygen obtained by electrolysis, after having been desiccated as thoroughly as possible, frequently yielded some water as a product of its decomposition by heat, yet that when certain precautions were taken, and certain sources of error in the production and collection of the electrolytic oxygen were recognized and avoided, a uniformly negative result was obtained, and not a trace of moisture or other compound of hydrogen resulted from the decomposition by heat of the ozone present in the oxygen.

This conclusion of Soret's was confirmatory both of the previous result of Andrews with regard also to electrolytically obtained ozone, and of the yet earlier result of Schönbein himself with regard to the ozone obtained by the slow oxidation of moist phosphorus. For in opposition to the view enunciated first by himself, and in seeming discrepancy with the undoubted fact that for the production of ozone by means of phosphorus the presence of moisture is essential, Schönbein, in 1849, showed by repeated experiment, that when ordinary air in quantities of several hundred litres, ozonized as strongly as possible by its passage over moist phosphorus, was transmitted first through a desiccating tube, then through a tube heated to 400° , so as to effect the destruction of the ozone present, and finally through another desiccating tube to absorb any moisture that might result from the destruction of the ozone, this last desiccating tube did not show, by an increase of weight or other change, any absorption of moisture whatever, notwithstanding the largeness of the absolute quantity of ozone destroyed in the experiment. From this time forth, Schönbein abandoned the notion of hydrogen being a constituent of ozone; and while making a valid distinction between his own view and that of Marignac and De la Rive, admitted with them that the matter of ozone is identical with the matter of oxygen. These last-named investigators, in their research already referred to (1845), showed that perfectly dry oxygen, submitted to the influence of electric discharges, experienced an alteration of character, whereby it acquired the property of liberating iodine from moist iodide of potassium,—a result

afterwards confirmed by Fremy and Becquerel. But they did not regard this alteration of character as due to the formation in small proportion of a new substance within the mass of oxygen, but rather to the assumption by the mass of oxygen of a peculiar electric condition. Moreover, the fact of dry oxygen being capable of some modification by the action of electric discharges, coupled with the fact of the inability of the so modified oxygen to act upon iodide of potassium save in the presence of water, was not inconsistent with the notion of this modified oxygen having to unite with water in order to produce a compound identical with the ozone obtained immediately from moist or watery reagents. That the effect of electrical discharges, and more particularly of the silent discharge, on perfectly dry oxygen, is really to convert a small proportion of this oxygen into ozone identical with that furnished by electrolysis, and capable of acting upon certain substances, as mercury and iodine, when in the dry state, and on certain other substances, as iodide of potassium and metallic silver, only when in the moist state, was first put beyond question by Andrews and Tait, in a research next to be considered.

IV.

In the spring of 1860, Dr. Andrews and Prof. Tait made a joint communication to the Royal Society on the volumetric relations of ozone. The primary object of this research was to ascertain whether any, and if so what, alteration of volume took place in the conversion of a given quantity of oxygen into ozone. They thus attacked the problem from an entirely new point of view, and, with admirably directed pains and skill, succeeded in making probably the most important contribution hitherto made to an exact knowledge of the nature of the ozone. In their experiments, a quantity of perfectly pure and dry oxygen, contained in a straight glass tube with a pressure-gauge appendix, was ozonized by means of the silent electric discharge passed through the gas for some time. Coincidentally with the passage of the silent discharge through it, the quantity of gas contained in the glass tube was observed to undergo a marked contraction in volume. This contraction proceeded at first rapidly, but afterwards more slowly, till it attained a limit which, in one of their experiments, was estimated at one-twelfth the original volume of the gas. And as whenever the gas, contracted in this manner, was examined, it was found to be proportionately ozonic, the general fact was established that the production of ozone from ordinary oxygen is attended with a contraction in volume. The converse result was also obtained. It was found that when oxygen, contracted by the passage of the electric discharge, was exposed for a short time to the temperature of 270° – 300° , it was restored to its original volume. And as whenever the gas, re-expanded in this manner, was examined, it was found to be free from ozone, the general fact was established that the conversion of ozone into ordinary oxygen is attended with an expansion in volume. And

this alternate contraction of a given quantity of oxygen by exposure to prolonged electrization, with production of ozone, and re-expansion of the gas to its original volume by exposure to a temporary heat, with destruction of ozone, could be repeated an indefinite number of times. Now the only possible conclusion to be drawn from these experiments would appear to be that, the matter of ozone being identical with the matter of oxygen, ozone is oxygen in a denser form,—that is to say, in the form of a more complex unit. Some years afterwards, this conclusion was confirmed in a very interesting manner by Professor Tyndall, in the case of ozone obtained electrolytically. He found that the absorptivity for radiant heat of electrolytically obtained oxygen, when rich in ozone, was upwards of a hundred times greater than that of ordinary oxygen—a result indicating ozone to have a more complex molecular constitution, and consequently a greater density, than ordinary oxygen. Moreover, after this same electrolytically obtained and richly ozonic oxygen had been subjected to the action of heat, so as to have its ozonic character destroyed, it then exhibited merely the absorptivity for heat of ordinary oxygen,—the observed absorptivity not going at all beyond that of ordinary oxygen, as would have been the case if the ozone originally present in the electrolytic gas had been decomposed into ordinary oxygen and aqueous vapour.

Referring to the statement already made, that in Messrs. Andrews and Tait's experiments, the oxygen gas, more or less contracted by the electric discharge, was found to be proportionately ozonic, this point was ascertained in the following way:—A small thin glass bulb, containing a solution of iodide of potassium, was introduced into the oxygen-holding tube, prior to its being filled with the gas; which, after having been more or less contracted by the process of electrization, was next submitted to the action of the solution, released on the breaking, effected by concussion, of the small bulb wherein it was contained. And on estimating the quantity of iodine set free from the iodide of potassium solution by its reaction with the contracted gas, it was found to be the exact chemical equivalent of a weight of oxygen equal in volume to the amount of contraction which the original gas had experienced during the process of electrization; so that if in the process of electrization, there had been one, two, or three cubic centimètres of contraction, the quantity of iodine liberated was chemically equivalent to the weight of one, two, or three cubic centimètres of oxygen; whence it results that to ascertain the iodine-titre of the ozonized gas is to learn the contraction of the original gas effected by its electrization, or the correlative expansion of the electrized gas effected by its exposure to heat. In the case also of electrolytically obtained ozonized oxygen, it was shown firstly by Andrews and Tait, and subsequently by Soret, that the iodine-titre of the gas is the measure of its expansion by heat, consequent on the conversion of its constituent ozone into ordinary oxygen.

V.

It has just been remarked that in the action of the contracted gas on iodide of potassium solution, there is absorbed by the reagent, with equivalent liberation of iodine, a weight of oxygen corresponding to a volume equal to that of the original contraction; but very curiously, the absorption by the reagent of this weight of oxygen from the contracted gas was found by Messrs. Andrews and Tait not to produce any further contraction or alteration of its volume; or the weight of oxygen which acted on the iodide of potassium solution appeared to occupy no part of the volume of the contracted gas, its removal from the contracted gas by means of the reagent not effecting any alteration in that volume. Since this remarkable result was first announced by Messrs. Andrews and Tait in 1860, it has been abundantly confirmed by von Babo and Claus, by Soret, and by Sir Benjamin Brodie—the modes of experimenting adopted in the original investigation of Andrews and Tait and in the three subsequent investigations, being all different from one another. And moreover, not only has the fact been established by the four several investigations with regard to iodide of potassium, but by one or other of the investigations with regard also to iodine, to mercurous salts, to ferrous salts, to arsenites, and to ferrocyanides. So that, when a given volume of ozonized oxygen is allowed to act upon these different oxidizable bodies, the oxidation effected by the ozone present in the gas is found to be unattended by any diminution in the volume of the gas. An interpretation of this singular result was put forward by the speaker soon after the publication of Messrs. Andrews and Tait's experiments, to the following effect: Ozone being proved to be a condensed form of oxygen, it is clear that any volume of ozone will contain a greater weight of the matter of oxygen than is contained in the same volume of ordinary oxygen. And since in the action of ozone upon iodide of potassium, the volume of the reacting gas does not undergo any alteration, it is obvious that the oxidation effected must be effected by only so much of the matter of oxygen contained in the volume of ozone, as is in excess of the matter of oxygen contained in the same volume of ordinary oxygen. This interpretation, so far as it went, was considered to be demanded by Messrs. Andrews and Tait's experiments, as the only satisfactory explanation of them. With regard to the weight of the matter of oxygen contained in a given volume of ozone, in excess of the weight of the matter of oxygen contained in the same volume of ordinary oxygen, no data whatever existed to show what this weight really is. But relying upon the fact that the weight of oxygen contained in a standard volume of free oxygen is composed of two simple weights of the matter of oxygen, it was conjectured that the weight of oxygen contained in a standard volume of ozone might not improbably be constituted by an introduction into the standard volume of ordinary oxygen of another simple weight of oxygen—equal volumes of ozone, free oxygen, and nitric oxide, for example, being expressible

by the comparable formulæ O_3 , O_2 , and NO respectively. In accordance with this supposition, the action of ozonized gas upon iodide of potassium, &c., is explicable as follows:—The ozone which acts is decomposed into a weight of free oxygen equal in volume to the volume of the ozone, and into another weight of absorbed oxygen, assumed to be one-half of the former weight. The suggestion as to the standard volume of ozone being constituted thus of three simple weights of the matter of oxygen, was admittedly not a necessary deduction from the then known facts, which were indeed equally consistent with its being constituted of four, five, or six such weights; it was only the suggestion of the simplest possible constitution for ozone that was consistent with the facts.

A few years afterwards, in 1865–66, the probability of this being the real constitution of ozone was much strengthened by the results of some experiments conducted by Soret. Operating by a process very simple and ingenious, but scarcely calculated to afford precise results, Soret found that when electrolytically obtained ozonized oxygen was allowed to act upon oil of turpentine, the absorption of the ozone by the turpentine was attended by a diminution in the volume of the gas equal approximatively to twice the initial contraction,—as inferred, of course, from the iodine-titre of the ozonized gas, or from its permanent expansion after exposure to a temporary heat. Supposing the final diminution effected by the turpentine to have been exactly twice the initial contraction, inferred from the iodine-titre, it is clear, that while the original gas would have suffered altogether a diminution of three volumes, the ozonized gas would have suffered a diminution of only two volumes. Or there would have been ultimately abstracted from the original uncontracted gas three volumes of the matter of oxygen, occupying in the contracted or ozonized gas, submitted to the action of the turpentine, only the bulk of two volumes. But as a mean result of Soret's first set of five experiments, the final diminution effected by the turpentine was 2.40 times the original contraction; while, as a mean result of his second set of seven experiments, the final diminution was 1.81 times the original contraction. Assuming, however, ozone to have the constitution expressed by the symbol O_3 , its specific gravity, and consequently its diffusion-velocity, would approximate closely to the specific gravity and diffusion-velocity of carbonic acid gas, CO_2 ; and in 1867, Soret, in corroboration of his previous absorption results, satisfied himself that the diffusion-velocity of ozone really does approximate very closely to that of carbonic acid.

VI.

During the last few years, the quantitative reactions of ozone have been made the subject of an elaborate study by Sir Benjamin Brodie, whose results constitute indeed “a body of exact information as to the chemical properties of ozone, through which it may be hoped that this important question will be finally removed from the domain of

arbitrary speculation and brought within the precincts of science." In Brodie's experiments, a quantity of pure perfectly dry oxygen, after having been submitted to electrization by its passage through a modified form of Siemens' induction tube, carefully maintained at a low temperature, was collected in an oil of vitriol gas-holder, to the amount of four or five thousand cubic centimètres. From the store of ozonized gas thus collected, which was found to maintain its proportion of ozone without appreciable deterioration for some hours, portion after portion was allowed to pass into a pipette of about 250 c.c. capacity, by displacement of the oil of vitriol originally filling it; and successive equal volumes of the store of ozonized gas so measured off, were submitted one after another to the action of the same or of different reagents, by the passage of each pipetteful of gas through a small bulb-tube containing the reagent in solution. The gas, freed from all ozone by its passage through the reagent, was next received into a mercurial measuring cylinder, in which it was expanded to a definite volume; and then, by reading off the pressure at which it occupied this volume, its proper volume was ascertained. Finally, the difference between the capacity of the pipette and the volume obtained in the mercurial cylinder showed the volume of the gas absorbed by the reagent,—the weight of this gas being determined directly or indirectly by titrations of the reagent. Of course, very many points of detail in the construction and use of the apparatus had to be attended to, in order to ensure trustworthy results; but, both in its principle and general working, the process is exceedingly simple. One essential novelty consists in the application of that very useful instrument, the pipette, to the purposes of gas analysis; and by its aid, results having a degree of accuracy far greater than those furnished by any previous method of ozone investigation, were found to be obtainable with both speed and facility.

Operating, then, with the apparatus just described, Brodie has succeeded in establishing three perfectly definite classes of ozone-reactions,—the first of them including the instances previously made known by Andrews and Tait. In this first class of reactions, of which there are several distinct varieties, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen, is unattended by any diminution in the volume of the gas; or a volume of ozone $O^2 + x$, is resolved into an equal volume of free oxygen, and an indefinite weight of other oxygen, either absorbed or set free. This class of reactions accordingly does not afford any information as to the value of x , or, in other words, as to the relationship of the formula $O^2 + x$ to the formula O^2 .

$$\overbrace{O^2 + x}^{\text{Unit-volumes}} = O^2 + x \text{ O absorbed.}$$

In a second class of reactions, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen, is attended with

a diminution in the volume of the gas, equal to half the volume that the weight of oxygen absorbed would occupy in the free state. In this class of reactions, then, one of but two occurrences must happen: either the ozone present in the mixture of gases, is absorbed wholly without decomposition, in which case the density of ozone must be twice that of ordinary oxygen, and the formula O^{2+z} become O^4 ; or the ozone present in the mixture, is decomposed into half its volume of oxygen liberated, and into a quantity of oxygen, corresponding to its entire volume, absorbed; in which case the density of ozone must be one-and-a-half that of ordinary oxygen, and the formula O^{2+z} become O^3 .

$$\begin{array}{rcl} \text{Unit-volumes.} & & \\ \overbrace{O^{2+z}} & = & \text{nil} + 4 O \\ 2 (O^{2+z}) & = & O^2 + 4 O \end{array} \left. \vphantom{\begin{array}{rcl} \overbrace{O^{2+z}} & = & \text{nil} + 4 O \\ 2 (O^{2+z}) & = & O^2 + 4 O \end{array}} \right\} \text{absorbed.}$$

In a third class of reactions, the absorption or decomposition of the ozone present in a mixture of ozone and oxygen, is attended with a diminution in volume of the gas, equal to two-thirds the volume that the weight of oxygen absorbed would occupy in the free state; or the weight of the gas absorbed is to the weight of an equal volume of oxygen as 3 to 2. But consistently with this class of reactions, the density of ozone must necessarily be one-and-a-half times that of ordinary oxygen, and the formula O^{2+z} must become O^3 .

$$\begin{array}{rcl} \text{Unit-volumes.} & & \\ \overbrace{(O^{2+z})} & = & \text{nil} + 3 O. \end{array}$$

This last and most important class of reactions, by which the formula of ozone as O^3 , is put beyond question, was established by a long series of experiments, made chiefly with a neutral or but slightly alkaline solution of hyposulphite of soda, and in a few cases with oil of turpentine. As a result, the ratio of the entire diminution in volume suffered by the original oxygen, to the diminution in volume of the electrized or contracted oxygen effected by the reagent, was found to be, as a mean of twenty-seven concordant experiments made with the hyposulphite, 3.02 to 2.02; and as a mean of eight concordant experiments made with the turpentine, also as 3.02 to 2.02. But neither with the hyposulphite nor with the turpentine, could the weight of oxygen absorbed by the reagent be determined, otherwise than by a calculation from the alteration in volume of the gas. A direct determination, however, was effected in the case of a few experiments made with protochloride of tin, under conditions carefully considered and regulated so as to ensure a trustworthy result. And it was found, in these few experiments, that the weight of the matter of oxygen absorbed from the ozonized gas by the tin-salt, was almost exactly three times the weight of the matter of oxygen absorbed from the same gas by iodide of potassium,—the volume occupied by the weight of oxygen absorbed by the tin-salt

being almost exactly twice the volume proper to the weight of oxygen absorbed by the iodide of potassium.

Independently of the importance attaching to the actual determination of the density of ozone, Sir B. Brodie's result has a further interest for chemists, which it would be difficult to exaggerate. The principal of the elementary bodies, known to chemists in the gaseous or vaporous state, are hydrogen, chlorine and its congeners, oxygen, sulphur, nitrogen, phosphorus, arsenic, mercury, and cadmium. Now it is a fact that the weight of phosphorus or arsenic contained in any volume of phosphorus or arsenic vapour, is four times the weight of phosphorus or arsenic contained in the same volume of phosphoretted or arsenetted hydrogen, and of a host of other phosphoretted or arsenetted gases or vapours. It is also a fact that the weight of hydrogen, chlorine, oxygen, or nitrogen contained in any volume of each of these elementary gases, is twice the weight of hydrogen, chlorine, oxygen, or nitrogen contained in the same volume of a variety of hydrogenous, chlorinous, oxygenous, or nitrogenous compound gases. It is also a fact that the weight of mercury or cadmium contained in any volume of the vapour of either element, is identical with the weight of the element contained in the same volume of the vapour of all its hitherto examined volatile compounds. But now a variety of oxygen is shown to exist, the weight of any given volume of which is three times the weight of oxygen contained in the same volume of the simplest of oxygenous compounds respectively, thus:—

Unit-volumes.			
P ₄	O ₃	O ₂	Hg
PCl ₃	CO	NO	HgCl ₂ .

The question, then, naturally arises, how long will it be before another variety of oxygen is recognized, the weight of any given volume of which, like that of a given volume of phosphorus vapour, shall furnish the weight of the element contained in four such volumes of its several simplest compounds? And again, how long will it be before yet another variety of oxygen is recognized, the weight of any given volume of which, like that of any given volume of mercury vapour, shall furnish but the weight of the element contained in the same volume of its several simplest compounds? There is the strongest indirect reason for believing in the existence of such a unitary oxygen. For in its reactions, oxygen behaves as a sort of more active electro-negative counterpart of electro-positive mercury Hg; and like mercury Hg, and unlike hydrogen H₂, and chlorine Cl₂, it enjoys the property of adding itself to a pre-formed unit of substance by an indivisible proportion.

[W. O.]

Friday, February 21, 1873.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

PROFESSOR J. CLERK MAXWELL, M.A. F.R.S.

On Action at a Distance.

I HAVE no new discovery to bring before you this evening. I must ask you to go over very old ground, and to turn your attention to a question which has been raised again and again ever since men began to think.

The question is that of the transmission of force. We see that two bodies at a distance from each other exert a mutual influence on each other's motion. Does this mutual action depend on the existence of some third thing, some medium of communication, occupying the space between the bodies, or do the bodies act on each other immediately, without the intervention of anything else?

The mode in which Faraday was accustomed to look at phenomena of this kind differs from that adopted by many other modern inquirers, and my special aim will be to enable you to place yourselves at Faraday's point of view, and to point out the scientific value of that conception of *lines of force* which, in his hands, became the key to the science of electricity.

When we observe one body acting on another at a distance, before we assume that this action is direct and immediate, we generally inquire whether there is any material connection between the two bodies; and if we find strings, or rods, or mechanism of any kind, capable of accounting for the observed action between the bodies, we prefer to explain the action by means of these intermediate connections, rather than to admit the notion of direct action at a distance.

Thus, when we ring a bell by means of a wire, the successive parts of the wire are first tightened and then moved, till at last the bell is rung at a distance by a process in which all the intermediate particles of the wire have taken part one after the other. We may ring a bell at a distance in other ways, as by forcing air into a long tube, at the other end of which is a cylinder with a piston which is made to fly out and strike the bell. We may also use a wire; but instead of pulling it, we may connect it at one end with a voltaic battery, and

at the other with an electro-magnet, and thus ring the bell by electricity.

Here are three different ways of ringing a bell. They all agree, however, in the circumstance that between the ringer and the bell there is an unbroken line of communication, and that at every point of this line some physical process goes on by which the action is transmitted from one end to the other. The process of transmission is not instantaneous, but gradual; so that there is an interval of time after the impulse has been given to one extremity of the line of communication, during which the impulse is on its way, but has not reached the other end.

It is clear, therefore, that in many cases the action between bodies at a distance may be accounted for by a series of actions between each successive pair of a series of bodies which occupy the intermediate space; and it is asked, by the advocates of mediate action, whether, in those cases in which we cannot perceive the intermediate agency, it is not more philosophical to admit the existence of a medium which we cannot at present perceive, than to assert that a body can act at a place where it is not.

To a person ignorant of the properties of air, the transmission of force by means of that invisible medium would appear as unaccountable as any other example of action at a distance, and yet in this case we can explain the whole process, and determine the rate at which the action is passed on from one portion to another of the medium.

Why then should we not admit that the familiar mode of communicating motion by pushing and pulling with our hands is the type and exemplification of all action between bodies, even in cases in which we can observe nothing between the bodies which appears to take part in the action?

Here for instance is a kind of attraction with which Professor Guthrie has made us familiar. A disk is set in vibration, and is then brought near a light suspended body, which immediately begins to move towards the disk, as if drawn towards it by an invisible cord. What is this cord? Sir W. Thomson has pointed out that in a moving fluid the pressure is least where the velocity is greatest. The velocity of the vibratory motion of the air is greatest nearest the disk. Hence the pressure of the air on the suspended body is less on the side nearest the disk than on the opposite side, the body yields to the greater pressure, and moves toward the disk.

The disk, therefore, does not act where it is not. It sets the air next it in motion by pushing it, this motion is communicated to more and more distant portions of the air in turn, and thus the pressures on opposite sides of the suspended body are rendered unequal, and it moves towards the disk in consequence of the excess of pressure. The force is therefore a force of the old school—a case of *vis a tergo*—a shove from behind.

The advocates of the doctrine of action at a distance, however, have not been put to silence by such arguments. What right, say

they, have we to assert that a body cannot act where it is not? Do we not see an instance of action at a distance in the case of a magnet, which acts on another magnet not only at a distance, but with the most complete indifference to the nature of the matter which occupies the intervening space? If the action depends on something occupying the space between the two magnets, it cannot surely be a matter of indifference whether this space is filled with air or not, or whether wood, glass, or copper, be placed between the magnets.

Besides this, Newton's law of gravitation, which every astronomical observation only tends to establish more firmly, asserts not only that the heavenly bodies act on one another across immense intervals of space, but that two portions of matter, the one buried a thousand miles deep in the interior of the earth, and the other a hundred thousand miles deep in the body of the sun, act on one another with precisely the same force as if the strata beneath which each is buried had been non-existent. If any medium takes part in transmitting this action, it must surely make some difference whether the space between the bodies contains nothing but this medium, or whether it is occupied by the dense matter of the earth or of the sun.

But the advocates of direct action at a distance are not content with instances of this kind, in which the phenomena, even at first sight, appear to favour their doctrine. They push their operations into the enemy's camp, and maintain that even when the action is apparently the pressure of contiguous portions of matter, the contiguity is only apparent—that a space *always* intervenes between the bodies which act on each other. They assert, in short, that so far from action at a distance being impossible, it is the only kind of action which ever occurs, and that the favourite old *vis a tergo* of the schools has no existence in nature, and exists only in the imagination of schoolmen.

The best way to prove that when one body pushes another it does not touch it, is to measure the distance between them. Here are two glass lenses, one of which is pressed against the other by means of a weight. By means of the electric light we may obtain on the screen an image of the place where the one lens presses against the other. A series of coloured rings is formed on the screen. These rings were first observed and first explained by Newton. The particular colour of any ring depends on the distance between the surfaces of the pieces of glass. Newton formed a table of the colours corresponding to different distances, so that by comparing the colour of any ring with Newton's table, we may ascertain the distance between the surfaces at that ring. The colours are arranged in rings because the surfaces are spherical, and therefore the interval between the surfaces depends on the distance from the line joining the centres of the spheres. The central spot of the rings indicates the place where the lenses are nearest together, and each successive ring corresponds to an increase of about the 4000th part of a millimetre in the distance of the surfaces.

The lenses are now pressed together with a force equal to the

weight of an ounce; but there is still a measurable interval between them, even at the place where they are nearest together. They are not in optical contact. To prove this, I apply a greater weight. A new colour appears at the central spot, and the diameters of all the rings increase. This shows that the surfaces are now nearer than at first, but they are not yet in optical contact, for if they were, the central spot would be black. I therefore increase the weights, so as to press the lenses into optical contact.

But what we call optical contact is not real contact. Optical contact indicates only that the distance between the surfaces is much less than a wave-length of light. To show that the surfaces are not in real contact, I remove the weights. The rings contract, and several of them vanish at the centre. Now it is possible to bring two pieces of glass so close together, that they will not tend to separate at all, but adhere together so firmly, that when torn asunder the glass will break, not at the surface of contact, but at some other place. The glasses must then be many degrees nearer than when in mere optical contact.

Thus we have shown that bodies begin to press against each other whilst still at a measurable distance, and that even when pressed together with great force they are not in absolute contact, but may be brought nearer still, and that by many degrees.

Why, then, say the advocates of direct action, should we continue to maintain the doctrine, founded only on the rough experience of a pre-scientific age, that matter cannot act where it is not, instead of admitting that all the facts from which our ancestors concluded that contact is essential to action were in reality cases of action at a distance, the distance being too small to be measured by their imperfect means of observation?

If we are ever to discover the laws of nature, we must do so by obtaining the most accurate acquaintance with the facts of nature, and not by dressing up in philosophical language the loose opinions of men who had no knowledge of the facts which throw most light on these laws. And as for those who introduce ætherial, or other media, to account for these actions, without any direct evidence of the existence of such media, or any clear understanding of how the media do their work, and who fill all space three and four times over with æthers of different sorts, why the less these men talk about their philosophical scruples about admitting action at a distance the better.

If the progress of science were regulated by Newton's first law of motion, it would be easy to cultivate opinions in advance of the age. We should only have to compare the science of to-day with that of fifty years ago; and by producing, in the geometrical sense, the line of progress, we should obtain the science of fifty years hence.

The progress of science in Newton's time consisted in getting rid of the celestial machinery with which generations of astronomers had encumbered the heavens, and thus "sweeping cobwebs off the sky."

Though the planets had already got rid of their crystal spheres,

they were still swimming in the vortices of Descartes. Magnets were surrounded by effluvia, and electrified bodies by atmospheres, the properties of which resembled in no respect those of ordinary effluvia and atmospheres.

When Newton demonstrated that the force which acts on each of the heavenly bodies depends on its relative position with respect to the other bodies, the new theory met with violent opposition from the advanced philosophers of the day, who described the doctrine of gravitation as a return to the exploded method of explaining everything by occult causes, attractive virtues, and the like.

Newton himself, with that wise moderation which is characteristic of all his speculations, answered that he made no pretence of explaining the mechanism by which the heavenly bodies act on each other. To determine the mode in which their mutual action depends on their relative position was a great step in science, and this step Newton asserted that he had made. To explain the process by which this action is effected was a quite distinct step, and this step Newton, in his 'Principia,' does not attempt to make.

But so far was Newton from asserting that bodies really do act on one another at a distance, independently of anything between them, that in a letter to Bentley, which has been quoted by Faraday in this place, he says:—

"It is inconceivable that inanimate brute matter should, without the mediation of something else, which is not material, operate upon and affect other matter without mutual contact, as it must do if gravitation, in the sense of Epicurus, be essential and inherent in it. . . . That gravity should be innate, inherent, and essential to matter, so that one body can act upon another at a distance, through a vacuum, without the mediation of anything else, by and through which their action and force may be conveyed from one to another, is to me so great an absurdity, that I believe no man who has in philosophical matters a competent faculty of thinking can ever fall into it."

Accordingly, we find in his 'Optical Queries,' and in his letters to Boyle, that Newton had very early made the attempt to account for gravitation by means of the pressure of a medium, and that the reason he did not publish these investigations "proceeded from hence only, that he found he was not able, from experiment and observation, to give a satisfactory account of this medium, and the manner of its operation in producing the chief phenomena of nature."*

The doctrine of direct action at a distance cannot claim for its author the discoverer of universal gravitation. It was first asserted by Roger Cotes, in his preface to the 'Principia,' which he edited during Newton's life. According to Cotes, it is by experience that we learn that all bodies gravitate. We do not learn in any other way that they are extended, movable, or solid. Gravitation, therefore, has as much right to be considered an essential property of matter as extension, mobility, or impenetrability.

* Maclaurin's Account of Newton's Discoveries.

And when the Newtonian philosophy gained ground in Europe, it was the opinion of Cotes rather than that of Newton that became most prevalent, till at last Boscovich propounded his theory, that matter is a congeries of mathematical points, each endowed with the power of attracting or repelling the others according to fixed laws. In his world, matter is unextended, and contact is impossible. He did not forget, however, to endow his mathematical points with inertia. In this some of the modern representatives of his school have thought that he "had not quite got so far as the strict modern view of 'matter' as being but an expression for modes or manifestations of 'force.' " *

But if we leave out of account for the present the development of the ideas of science, and confine our attention to the extension of its boundaries, we shall see that it was most essential that Newton's method should be extended to every branch of science to which it was applicable—that we should investigate the forces with which bodies act on each other in the first place, before attempting to explain *how* that force is transmitted. No men could be better fitted to apply themselves exclusively to the first part of the problem, than those who considered the second part quite unnecessary.

Accordingly Caverish, Coulomb, and Poisson, the founders of the exact sciences of electricity and magnetism, paid no regard to those old notions of "magnetic effluvia" and "electric atmospheres," which had been put forth in the previous century, but turned their undivided attention to the determination of the law of force, according to which electrified and magnetized bodies attract or repel each other. In this way the true laws of these actions were discovered, and this was done by men who never doubted that the action took place at a distance, without the intervention of any medium, and who would have regarded the discovery of such a medium as complicating rather than as explaining the undoubted phenomena of attraction.

We have now arrived at the great discovery by Ørsted of the connection between electricity and magnetism. Ørsted found that an electric current acts on a magnetic pole, but that it neither attracts it nor repels it, but causes it to move round the current. He expressed this by saying that "the electric conflict acts in a revolving manner."

The most obvious deduction from this new fact was that the action of the current on the magnet is not a push-and-pull force, but a rotatory force, and accordingly many minds were set a-speculating on vortices and streams of æther whirling round the current.

But Ampère, by a combination of mathematical skill with experimental ingenuity, first proved that two electric currents act on one another, and then analysed this action into the resultant of a system of push-and-pull forces between the elementary parts of these currents.

* Review of Mrs. Somerville, 'Saturday Review,' Feb. 13, 1869.

The formula of Ampère, however, is of extreme complexity, as compared with Newton's law of gravitation, and many attempts have been made to resolve it into something of greater apparent simplicity.

I have no wish to lead you into a discussion of any of these attempts to improve a mathematical formula. Let us turn to the independent method of investigation employed by Faraday in those researches in electricity and magnetism which have made this Institution one of the most venerable shrines of science.

No man ever more conscientiously and systematically laboured to improve all his powers of mind than did Faraday from the very beginning of his scientific career. But whereas the general course of scientific method then consisted in the application of the ideas of mathematics and astronomy to each new investigation in turn, Faraday seems to have had no opportunity of acquiring a technical knowledge of mathematics, and his knowledge of astronomy was mainly derived from books.

Hence, though he had a profound respect for the great discovery of Newton, he regarded the attraction of gravitation as a sort of sacred mystery, which, as he was not an astronomer, he had no right to gainsay or to doubt, his duty being to believe it in the exact form in which it was delivered to him. Such a dead faith was not likely to lead him to explain new phenomena by means of direct attractions.

Besides this, the treatises of Poisson and Ampère are of so technical a form, that to derive any assistance from them the student must have been thoroughly trained in mathematics, and it is very doubtful if such a training can be begun with advantage in mature years.

Thus Faraday, with his penetrating intellect, his devotion to science, and his opportunities for experiments, was debarred from following the course of thought which had led to the achievements of the French philosophers, and was obliged to explain the phenomena to himself by means of a symbolism which he could understand, instead of adopting what had hitherto been the only tongue of the learned.

This new symbolism consisted of those lines of force extending themselves in every direction from electrified and magnetic bodies, which Faraday in his mind's eye saw as distinctly as the solid bodies from which they emanated.

The idea of lines of force and their exhibition by means of iron filings was nothing new. They had been observed repeatedly, and investigated mathematically as an interesting curiosity of science. But let us hear Faraday himself, as he introduces to his reader the method which in his hands became so powerful.*

"It would be a voluntary and unnecessary abandonment of most valuable aid if an experimentalist, who chooses to consider magnetic power as represented by lines of magnetic force, were to deny himself the use of iron filings. By their employment he may make many conditions of the power, even in complicated cases, visible to the eye

at once, may trace the varying direction of the lines of force and determine the relative polarity, may observe in which direction the power is increasing or diminishing, and in complex systems may determine the neutral points, or places where there is neither polarity nor power, even when they occur in the midst of powerful magnets. By their use probable results may be seen at once, and many a valuable suggestion gained for future leading experiments."

Experiment on Lines of Force.

In this experiment each filing becomes a little magnet. The poles of opposite names belonging to different filings attract each other and stick together, and more filings attach themselves to the exposed poles, that is, to the ends of the row of filings. In this way the filings, instead of forming a confused system of dots over the paper, draw together, filing to filing, till long fibres of filings are formed, which indicate by their direction the lines of force in every part of the field.

The mathematicians saw in this experiment nothing but a method of exhibiting at one view the direction in different places of the resultant of two forces, one directed to each pole of the magnet; a somewhat complicated result of the simple law of force.

But Faraday, by a series of steps as remarkable for their geometrical definiteness as for their speculative ingenuity, imparted to his conception of these lines of force a clearness and precision far in advance of that with which the mathematicians could then invest their own formulæ.

In the first place, Faraday's lines of force are not to be considered merely as individuals, but as forming a system, drawn in space in a definite manner, so that the number of the lines which pass through an area, say of one square inch, indicates the intensity of the force acting through the area. Thus the lines of force become definite in number. The strength of a magnetic pole is measured by the number of lines which proceed from it; the electro-tonic state of a circuit is measured by the number of lines which pass through it.

In the second place, each individual line has a continuous existence in space and time. When a piece of steel becomes a magnet or when an electric current begins to flow, the lines of force do not start into existence each in its own place, but as the strength increases new lines are developed within the magnet or current, and gradually grow outwards, so that the whole system expands from within, like Newton's rings in our former experiment. Thus every line of force preserves its identity during the whole course of its existence, though its shape and size may be altered to any extent.

I have no time to describe the methods by which every question relating to the forces acting on magnets or on currents, or to the induction of currents in conducting circuits, may be solved by the consideration of Faraday's lines of force. In this place they can

never be forgotten. By means of this new symbolism, Faraday defined with mathematical precision the whole theory of electro-magnetism, in language free from mathematical technicalities, and applicable to the most complicated as well as the simplest cases. But Faraday did not stop here. He went on from the conception of geometrical lines of force to that of physical lines of force. He observed that the motion which the magnetic or electric force tends to produce is invariably such as to shorten the lines of force and to allow them to spread out laterally from each other. He thus perceived in the medium a state of stress, consisting of a tension, like that of a rope, in the direction of the lines of force, combined with a pressure in all directions at right angles to them.

This is quite a new conception of action at a distance, reducing it to a phenomenon of the same kind as that action at a distance which is exerted by means of the tension of ropes and the pressure of rods. When the muscles of our bodies are excited by that stimulus which we are able in some unknown way to apply to them, the fibres tend to shorten themselves and at the same time to expand laterally. A state of stress is produced in the muscle, and the limb moves. This explanation of muscular action is by no means complete. It gives no account of the cause of the excitement of the state of stress, nor does it even investigate those forces of cohesion which enable the muscles to support this stress. Nevertheless, the simple fact, that it substitutes a kind of action which extends continuously along a material substance for one of which we know only a cause and an effect at a distance from each other, induces us to accept it as a real addition to our knowledge of animal mechanics.

For similar reasons we may regard Faraday's conception of a state of stress in the electro-magnetic field as a method of explaining action at a distance by means of the continuous transmission of force, even though we do not know how the state of stress is produced.

But one of Faraday's most pregnant discoveries, that of the magnetic rotation of polarized light, enables us to proceed a step farther. The phenomenon, when analysed into its simplest elements, may be described thus:—Of two circularly polarized rays of light, precisely similar in configuration, but rotating in opposite directions, that ray is propagated with the greater velocity which rotates in the same direction as the electricity of the magnetizing current.

It follows from this, as Sir W. Thomson has shown by strict dynamical reasoning, that the medium when under the action of magnetic force must be in a state of rotation—that is to say, that small portions of the medium, which we may call molecular vortices, are rotating, each on its own axis, the direction of this axis being that of the magnetic force.

Here, then, we have an explanation of the tendency of the lines of magnetic force to spread out laterally and to shorten themselves. It arises from the centrifugal force of the molecular vortices.

The mode in which electromotive force acts in starting and stop-

ping the vortices is more abstruse, though it is of course consistent with dynamical principles.

We have thus found that there are several different kinds of work to be done by the electro-magnetic medium if it exists. We have also seen that magnetism has an intimate relation to light, and we know that there is a theory of light which supposes it to consist of the vibrations of a medium. How is this luminiferous medium related to our electro-magnetic medium?

It fortunately happens that electro-magnetic measurements have been made from which we can calculate by dynamical principles the velocity of propagation of small magnetic disturbances in the supposed electro-magnetic medium.

This velocity is very great, from 288 to 314 millions of mètres per second, according to different experiments. Now the velocity of light, according to Foucault's experiments, is 298 millions of mètres per second. In fact, the different determinations of either velocity differ from each other more than the estimated velocity of light does from the estimated velocity of propagation of small electro-magnetic disturbance. But if the luminiferous and the electro-magnetic media occupy the same place, and transmit disturbances with the same velocity, what reason have we to distinguish the one from the other? By considering them as the same, we avoid at least the reproach of filling space twice over with different kinds of æther.

Besides this, the only kind of electro-magnetic disturbances which can be propagated through a non conducting medium is a disturbance transverse to the direction of propagation, agreeing in this respect with what we know of that disturbance which we call light. Hence, for all we know, light also may be an electro-magnetic disturbance in a non-conducting medium. If we admit this, the electro-magnetic theory of light will agree in every respect with the undulatory theory, and the work of Thomas Young and Fresnel will be established on a firmer basis than ever, when joined with that of Cavendish and Coulomb by the keystone of the combined sciences of light and electricity. Faraday's great discovery of the electro-magnetic rotation of light.

The vast interplanetary and interstellar regions will no longer be regarded as waste places in the universe, which the Creator has not seen fit to fill with the symbols of the manifold order of His kingdom. We shall find them to be already full of this wonderful medium: so full, that no human power can remove it from the smallest portion of space, or produce the slightest flaw in its infinite continuity. It extends unbroken from star to star; and when a molecule of hydrogen vibrates in the dogstar, the medium receives the impulses of these vibrations; and after carrying them in its immense bosom for three years, delivers them in due course, regular order, and full tale into the spectroscope of Mr. Huggins, at Tulse Hill.

But the medium has other functions and operations besides bearing light from man to man, and from world to world, and giving

evidence of the absolute unity of the metric system of the universe. Its minute parts may have rotatory as well as vibratory motions, and the axes of rotation form those lines of magnetic force which extend in unbroken continuity into regions which no eye has seen, and which, by their action on our magnets, are telling us in language not yet interpreted, what is going on in the hidden underworld from minute to minute and from century to century.

And these lines must not be regarded as mere mathematical abstractions. They are the directions in which the medium is exerting a tension like that of a rope, or rather, like that of our own muscles. The tension of the medium in the direction of the earth's magnetic force is in this country one grain weight on eight square feet. In some of Dr. Joule's experiments, the medium has exerted a tension of 200 lbs. weight per square inch.

But the medium, in virtue of the very same elasticity by which it is able to transmit the undulations of light, is also able to act as a spring. When properly wound up, it exerts a tension, different from the magnetic tension, by which it draws oppositely electrified bodies together, produces effects through the length of telegraph wires, and when of sufficient intensity, leads to the rupture and explosion called lightning.

These are some of the already discovered properties of that which has often been called vacuum, or nothing at all. They enable us to resolve several kinds of action at a distance into actions between contiguous parts of a continuous substance. Whether this resolution is of the nature of explication or complication, I must leave to the metaphysicians.

[J. C. M.]

Friday, May 2, 1873.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

DR. J. EMERSON REYNOLDS,

PROFESSOR OF CHEMISTRY, ROYAL DUBLIN SOCIETY, AND CHIEF OF THE MINERAL DEPARTMENT,

On Alcohols from Flint and Quartz.

IN appearing before you this evening to lecture on "Alcohols from Flint and Quartz," you will permit me at the outset to explain, and even materially to extend, the title of my discourse.

I do not propose to show that spirits can be extracted from flint and quartz by mechanical processes; but I hope to satisfy you that by indirect and purely chemical means we can obtain from these familiar and widely-diffused minerals, and from native silicates, bodies resembling in chemical action, and even in appearance, the well-known alcohol of wine.

Carbon has hitherto been considered the sole alcohol-forming element; but we shall see that the chief constituent of flint and quartz, namely, silicon, must now be admitted to share in this power, and likewise in the ability to form other remarkable compounds that it will be necessary for me to refer to in the course of this lecture.

In selecting this subject, I have done so in part because this most promising field of research, opened up by the labours of Wohler, Buff, Friedel, Crafts, Ladenburg, and others, has hitherto been but little cultivated in this country, and therefore probably possesses some novelty for the audience I have the honour to address; and also because we find in this new branch of chemical investigation most interesting illustrations of the advantage we may derive from the cautious use of the argument from analogy.

As a preliminary to the inquiry I propose, we may consider very briefly the chemical nature of flint and quartz.

The word "flint" is of very ancient origin, and was often used to indicate any particularly hard rock. In this sense it is employed several times in the Old Testament—first, in the Book of Deuteronomy, viii. 15, and in Psalms, cxiv. 8, where the rock struck by Moses is said to be "of flint." We now use the term to distinguish a well-known uncrystalline mineral, which can be easily shown to be a chemical compound of two so-called elementary forms of matter—oxygen and silicon.

Flint is identical in chemical composition with quartz or rock-crystal, though physically different, as you will perceive by reference to the fine specimens on the table, kindly lent by Mr. Bryce

M. Wright, the well-known mineral collector. The common name of "silica" is given to the chemical compound, and the terms flint, agate, quartz, rock-crystal, are reserved for the forms in which we meet with this remarkable substance in nature.

Having cleared our ground so far, we have to find how the oxygen may be separated from any of those forms of silica, and the element silicon may be obtained. This cannot be directly accomplished, but by indirect means we can obtain the desired results. I have here a quantity of finely-divided flint mixed with some powdered fluor-spar; when I pour oil of vitriol on the mixture, and apply heat, a colourless gas is obtained, which, when passed into water, produces a highly acid and gelatinous liquid. The gas is a compound of the element fluorine, with silicon—the tetrafluoride of silicon—and this, when brought in contact with water, produces an acid called hydrofluosilicic and a quantity of gelatinous hydrate of silica.

The clear acid liquid, when treated with caustic soda, yields this white salt, the fluosilicate of sodium, from which we directly obtain the silicon, as you see, by simply heating with some metallic sodium. In this case, the sodium replaces the silicon, the latter separating, as you observe, in the tube as a dark brown substance.

Having thus prepared silicon from flint, we are in a position to compare it with carbon, to trace out the analogies which subsist between them, and then to show that some of the alcoholic and other compounds of carbon have their strange and interesting analogues in a silicon series.

First, then, we shall compare the elements themselves.

We meet with nearly pure carbon under the well-known forms of charcoal, graphite, and diamond.

We can easily prepare the corresponding varieties of silicon—the amorphous, the graphitoid, and adamantine. With the aid of the phengascope, I shall now project on the screen images of specimens, in order that you may compare the varieties side by side. I have also on the table a very fine specimen of crystallized silicon, for which I have to thank Messrs. Hopkin and Williams. [The lecturer showed a greatly magnified image of a fine crystallized diamond on the screen; a number of other specimens were exhibited in the same way.]

As might be anticipated, the specific gravity of carbon is lowest in charcoal and highest in diamond. Corresponding differences in specific gravity are observed between the varieties of silicon. The two elements also correspond remarkably in variations of specific heat, with different states of aggregation. The specific heat of the diamond is lower than that of graphite, and the specific heat of adamantine silicon is lower than that of the graphitoid variety.

Passing now from the points of physical resemblance between carbon and silicon, I shall dwell more particularly on the chemical relations of the two elements.

We are familiar with the fact that carbon burns in oxygen, producing, in an excess of that gas, the well-known gaseous oxide of

carbon, commonly called carbonic acid; charcoal or coke burn readily in oxygen, while graphite is consumed with considerable difficulty, and the diamond is still more difficult of combustion. Amorphous silicon burns as easily in oxygen as charcoal, and forms the oxide silica, the same oxide that we find as flint or quartz. [Experiments exhibited.]

In this way we can reproduce, so far as composition is concerned, the substance from which we originally obtained the silicon for our experiments. Now, though amorphous silicon is easily burnt, the graphitic and adamantine varieties of the element resemble the corresponding forms of carbon in difficult combustibility. Crystalline silicon may be raised even to a white heat in oxygen gas without burning.

Unlike carbon, silicon in any of its forms easily combines directly with chlorine, producing the liquid chloride which I have in this tube. This is a very volatile body, boiling at 50° C., and is half as heavy again as water. It can also be prepared from silica by heating to full redness the finely-divided oxide and carbon in a current of chlorine. In composition this chloride is the silicon representative of tetrachloride of carbon.

In addition to this chloride of silicon, the discovery of which we owe to Berzelius, another has very recently been obtained by Friedel, which corresponds to a well-known carbon hexachloride.

We next pass to a compound of silicon with hydrogen. It may be prepared in a pure state by means of a rather complex reaction I shall have presently to refer to; but we can easily obtain the impure gas by Wohler's method, in treating a compound of silicon and magnesium with hydrochloric acid. We thus obtain a colourless, spontaneously inflammable gas, which burns with a bright light on contact with the air. In its pure condition, siliciuretted hydrogen is not spontaneously combustible at ordinary pressure, but in a slightly rarefied atmosphere it easily inflames. The compositions of these silicon and carbon compounds are shown in this table:—

SiO_2	Oxides	CO_2
SiCl_4	Chlorides.	CCl_4
Si_2Cl_6	"	C_2Cl_6
SiH_4	Hydrides.	CH_4

The siliciuretted hydrogen is evidently the chemical analogue of marsh-gas, the tetrahydride of carbon.

It is usual to regard marsh-gas as the typical carbon compound from which some alcoholic series may be supposed to spring, and, in fact, all the alcohols belonging to the group of which the well-known wood-spirit and spirit of wine are the chief members, are commonly regarded as derivatives of marsh-gas, in which a part, or all, the hydrogen has been replaced by one or more compound radicals, such as hydroxyl, methyl, ethyl, propyl, &c. In these cases, carbon of the marsh-gas is the grouping element of the compound, or that con-

stituent which serves to bind together the different materials of which the molecular edifice is constructed. In the same way the silicon in siliciuretted hydrogen may be shown to be the nucleus round which can be grouped hydroxyl, methyl, ethyl, &c., so as to form the alcohols whose compositions I shall presently have to refer to. Several of the less complex terms are still wanting, but their existence is rendered highly probable by the occurrence of bodies bearing the same close relation to the unknown alcohol that marsh-gas bears to wood-spirit, or the acid of vinegar (acetic acid) to common spirit of wine. As we ascend in the series, however, we meet with the true alcohols, in which silicon takes the place of carbon as the grouping element.

It must be here admitted, however, that no well-defined alcohols have yet been discovered in which silicon acts in any other way than as the nucleus of the compound; carbon radicals in all these cases playing the subordinate parts. But we have every reason to expect that complex alcohols containing silicon only will yet be obtained as researches extend.

In 1857 Buff and Wohler obtained a volatile fuming liquid on heating crystalline silicon nearly to redness in a current of dry hydrochloric acid gas. The precise nature of this liquid was unknown until 1871, when Friedel and Crafts published the results of their admirable researches upon Buff and Wohler's liquid, and showed that it was a mixture of chloride of silicon with a new body, which proved to be the strict chemical analogue of our well-known chloroform, silicon replacing carbon.



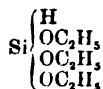
Chloroforms.



This body is a colourless, mobile, and very volatile liquid boiling at 35°C . I have a quantity of it in this tube. One of its most remarkable properties is that of exploding with great facility when its vapour is mixed with air. I shall now show you the experiment. Ordinary chloride of silicon does not afford an explosive mixture when its vapour is mingled with air. [Experiments shown.]

When this remarkable body is made to unite with anhydrous alcohol, a colourless ethereal liquid is obtained on distillation, having an agreeable odour, and a boiling-point at 131°C . This body is strictly analogous in composition to a substance obtained by Williamson and Kay, by acting on ordinary chloroform with sodium alcohol.

These ethers may each be regarded as derived from a glycerine or triatomic alcohol, as shown below. Neither of these alcohols has as yet been isolated.



Formic ethers (tribasic).



Glycerins.



By the action of sodium on the silicon ether just referred to we can obtain siliciuretted hydrogen in a state of purity. This is the only known mode of obtaining the pure compound.

Returning to the silicon chloroform, about whose chemical nature we can now have little if any doubt, we next have to inquire in what direction, and how far, we can pursue the analogy between the great pain-killer, discovered almost simultaneously by Soubeiran and the illustrious chemist of Giessen, who has so recently passed away from amongst us, and the curious body that we can obtain indirectly from flint or other form of silica in the manner I have described.

Ordinary chloroform is well known to be closely allied to common wood-spirit, or methyl alcohol, in a way that will be evident on comparing the formulæ. In fact, chloroform is easily obtained by treating wood-spirit with bleaching-powder. We cannot in any simple way reverse this process and prepare wood-spirit from chloroform, but we can do something in this direction, for we are able by the action of caustic potash to obtain from chloroform formic acid, a body which is one of the most remarkable products of oxidation of wood-spirit. The relation of formic acid to the alcohol is shown in the table below; and it is there further pointed out that this formic acid should yield an anhydride—a body capable of producing the acid by union with the elements of water. This anhydride is not known, but the importance of suggesting its existence will appear in a moment.

Si	$\begin{cases} \text{H} \\ \text{H} \\ \text{H} \\ \text{OH} \end{cases}$	Methyl alcohols.	C	$\begin{cases} \text{H} \\ \text{H} \\ \text{H} \\ \text{OH} \end{cases}$
Si	$\begin{cases} \text{H} \\ \text{O} \\ \text{OH} \end{cases}$	Formic acids.	C	$\begin{cases} \text{H} \\ \text{O} \\ \text{OH} \end{cases}$
Si	$\begin{cases} \text{H} \\ \text{O} \\ \text{O}(\text{SiOH}) \end{cases}$	Anhydrides.	C	$\begin{cases} \text{H} \\ \text{O} \\ \text{O}(\text{COH}) \end{cases}$

Regarding silicon chloroform from the same point of view, analogy would lead us to look for a simple silicon alcohol similar to wood-spirit or methyl alcohol; but we would not expect the silicon chloroform easily to yield this alcohol directly, though we would be justified in hoping that an acid, corresponding to formic acid, might be obtained. As a matter of fact, no such alcohol has as yet been prepared even indirectly; but a corresponding acid is very readily produced, and more than this, for the anhydride at present wanting in the carbon series is found in that of silicon. If I pass the vapour of silicon chloroform into water nearly ice-cold, a white solid body is obtained without any evolution of hydrogen, and an acid liquid produced. The white solid then collected, washed, and dried at a low temperature, forms a white inflammable powder, which was first described by Buff and Wohler. Friedel and Ladenburg have shown that this remarkable body is the anhydride of the silico-formic acid. According to the

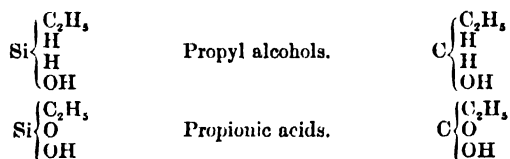
results of my own investigations, the acid liquid to which I referred just now contains, in addition to hydrochloric acid, the true silico-formic acid—a body possessing nearly as energetic reducing properties as the corresponding acid derived from wood-spirit. I shall now demonstrate these facts. [The lecturer then exhibited the experiments referred to.]

It will naturally be asked whether the silicon chloroform is capable of acting as an anæsthetic like ordinary chloroform. But it is only necessary to bear in mind the fact that it is very easily decomposed by water into gelatinous matter, and highly corrosive hydrochloric acid, in order to understand that its inhalation would be attended by the speedy destruction of the lungs of any person persisting in the experiment.

Starting from silicon chloroform, then, we have been led, by analogical reasoning in the first instance, to infer the existence of a simple silicon alcohol precisely corresponding to wood-spirit. On testing this induction by experiment, we have obtained answers which are, so far as they go, altogether favourable to the view just stated. In fact, the results are as satisfactory as they can be short of the discovery of the silico-methyl alcohol.

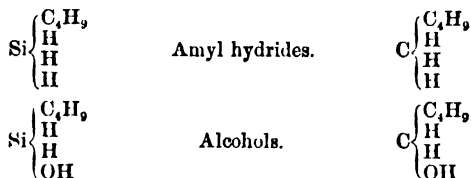
I shall now endeavour to strengthen this position by showing that the existence of three higher members of the alcoholic series has been rendered highly probable by the discovery of closely-related bodies, though the alcohols themselves have not been isolated; and, finally, I shall show that the alcohols of still higher terms have actually been obtained.

In the course of their elaborate and able investigation of silicon compounds, Friedel and Crafts discovered that chloride of silicon easily acts upon common alcohol, as I have already mentioned, producing a body which Friedel and Ladenburg have recently shown to be easily attacked by a mixture of sodium with a curious substance contained in this tube—zinc-ethyl. The product, when treated with caustic potash, yields a body which bears the same relation to silico-propyl alcohol that formic acid does to wood-spirit. This relationship is shown in the formulæ—

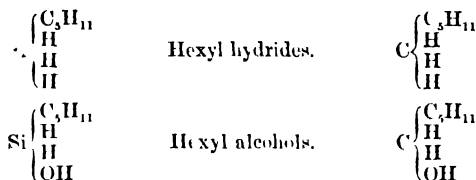


This silico-propionic acid is in this tube, and is a white combustible powder, like the silico-formic anhydride I have already shown to you. It is soluble in warm caustic potash, but not in caustic soda; by which character it can be distinguished from silica. It is only necessary to state that it can be obtained in aqueous solution, and in the pure state, by Professor Graham's valuable dialytic process.

In the amyl term, neither alcohol nor acid are yet known ; but by the action of zinc-methyl on chloride of silicon we can obtain a light, colourless, and very volatile liquid, which is silicon-methide, a body that may, for reasons which will presently appear, be fairly considered to stand in the same relation to silico-amyl alcohol that marsh-gas does to wood-spirit. Thus—

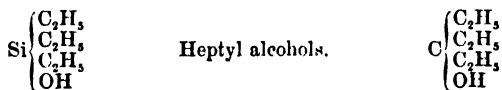


The researches of Friedel and Crafts have made us acquainted with a body which may also probably be regarded as the hydride corresponding to silico-hexyl alcohol. This compound is prepared by the action of zinc-methide and zinc-ethide in chloride of silicon.



Having, therefore, stated the grounds for inferring the existence of silico-propyl, silico-amyl, and silico-hexyl alcohols, I shall now pass at once to the second class of evidence, and show that the alcohols of still higher terms can actually be prepared.

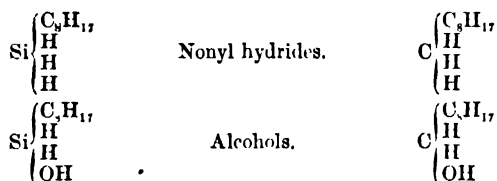
In referring to the preparation of silico-propionic acid, it was stated that when chloride of silicon acts upon absolute alcohol a body is obtained which, on treatment with zinc-ethyl and sodium, yields an ethereal product from which silico-propionic acid can be obtained by treatment with caustic potash. If, however, instead of using the caustic alkali we continue the action of zinc-ethyl and sodium, decompose the products with water in sealed tubes, and distil, a liquid is obtained which contains one of the "alcohols from flint" we are in search of. In this tube I have a small quantity of the alcohol, and here you will find its composition stated—



You will observe that it is the silico-heptyl alcohol precisely corresponding to a simple carbon alcohol recently discovered by Nahapetian, both being *tertiary* alcohols. We owe to Ladenburg the discovery of this lowest known term of alcohols containing silicon.

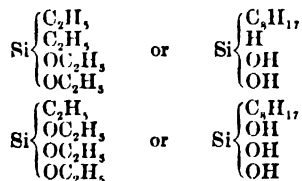
As you can observe it is a colourless liquid, not unlike the ordinary alcohol of wine. It is insoluble in water, but easily dissolved by spirit and ether. Chemically it acts just like any of the other alcohols, producing ethers, and dissolving the alkali metals to form sodium or potassium alcoholates. When common spirit burns you are aware that its flame is nearly colourless, but I shall now burn some of our alcohol from flint, and you will find, particularly when we feed the flame with oxygen, that a bright light is emitted.

Clearly defined though this alcohol is, it does not stand alone, for at least one other compound of the same order is known. It was suggested in 1870, by Friedel and Crafts, that silicon ethide—a body easily prepared by the action of chloride of silicon on zinc ethide—might be regarded as the hydride of silico-nonyl, and should stand in the same relation to an alcohol that marsh-gas does to common wood-spirit, or ethyl hydride to ordinary alcohol. This happy idea, when put to the test of experiment, was fully justified by the result, for, on treating silicon ethide in essentially the same manner that we should adopt in preparing wood-spirit from marsh-gas, a colourless liquid, lighter than, and insoluble in, water is obtained. The boiling point of this body is 190° C. It yields an ether with acetic acid, dissolves sodium, forming an alcoholate, and, in fact, conforms to the general habits of the alcohols of the series to which common spirit belongs. The compositions of these bodies are thus represented—



It is thus shown to be precisely similar to the nonyl alcohol prepared by Pelouze and Cahours from American petroleum.

Ladenburg has very recently advanced even beyond the point we have now reached, and has shown that the chloride of silicon can be made to yield two ethers, which correspond, as I may suggest, to silico-nonyl diatomic and triatomic alcohols. Thus—



In all the preceding compounds it will have been noted that but one atom of silicon is present, and though, as I pointed out in the earlier part of this lecture, the silicon in these cases occupies the

chief position as the grouping element, we should much like to see silicon uniting with silicon, and forming a more condensed compound with hydrogen. Happily, however, very important evidence, even upon this point, is forthcoming, for Friedel and Ladenburg have discovered corresponding hexa-chloride, iodide, and bromide of silicon, and treatment of the hexa-iodide with zinc-ethyl enables us to obtain the ethide whose formula is given in this table—

Hydride.	Chloride.	Ethide.
$\begin{array}{c} \text{Si} \left\{ \begin{array}{l} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \right. \\ \text{Si} \left\{ \begin{array}{l} \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \right. \end{array}$	$\begin{array}{c} \text{Si} \left\{ \begin{array}{l} \text{Cl} \\ \text{Cl} \\ \text{Cl} \\ \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{array} \right. \\ \text{Si} \left\{ \begin{array}{l} \text{Cl} \\ \text{Cl} \\ \text{Cl} \\ \text{Cl} \\ \text{Cl} \\ \text{Cl} \end{array} \right. \end{array}$	$\begin{array}{c} \text{Si} \left\{ \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right. \\ \text{Si} \left\{ \begin{array}{l} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{array} \right. \end{array}$

It is not improbable that in the last-named compound we have the starting-point of a new series of still more complex bodies, analogous to derivatives of olefiant-gas rather than to those of marsh-gas.

I trust you will now admit that the case I proposed to lay before you has been made out—namely, that we can obtain some alcohols indirectly from flint or other form of silica, and that we have solid ground for inferring the existence of many others.

A rich and beautiful field for chemical research appears to lie before us in tracing out the analogies between the compounds of carbon and silicon, and recognising the chemical representatives of many of the most complex “organic compounds” in the native silicates which form so large a part of the crust of this earth.

Hitherto in this lecture I have avoided reference to subjects not directly connected with the matter in hand, but, before concluding, I would refer, necessarily in a very few words, to some inquiries in this department of chemistry which have been carried on in the laboratory of the Royal Dublin Society. First, however, allow me to perform an experiment. I have here a glass jar filled with dry ammoniacal gas; when I drop it into some chloride of silicon, a white compound is obtained. This body was discovered by Persoz in 1830, and the composition he assigns to it would, as ably suggested by Dr. Hofmann, represent a mixture of sal-ammoniac with the hydrochlorate of silicon-guanidine. If this white body be ignited strongly in a closed vessel, an infusible white substance remains, which has been examined by Deville and Wöhler, who have shown that it contains silicon and nitrogen, and that the same or similar body can be produced by intensely heating crystalline silicon in an atmosphere of nitrogen.

My examination of this curious body has led me to the conclusion that it is the silicon analogue of cyanogen—a well-known compound of nitrogen with carbon, and the chief constituent of the deadly poison prussic acid. This body, though little affected even at a very high temperature, in the absence of moisture is easily decomposed by steam—silica, ammonia, and hydrogen resulting. A similar decompo-

sition is effected by heating with soda-lime. I may add that, when this singular compound is fused with a small quantity of carbonate of potassium, cyanide and silicate of the metal are produced; in this case, carbon appears to displace silicon.

If, in the experiments with ammoniacal gas, we substitute silicon chloroform for the silicic chloride, a body is obtained from which this compound of silicon and nitrogen can be easily extracted. Now we know well that when ordinary chloroform is heated with ammonia gas, chloride and cyanide of ammonium are obtained, and that under certain circumstances a body called *para-cyanogen* is also produced. Analogy would lead us to anticipate that silicon chloroform would react in a similar manner, and the facts I have hitherto observed justify this inference.

It would be out of place to pursue this subject here, as the results of the inquiry referred to have not yet been published. I have, therefore, now simply shown to you one of the chief bodies to which interest belongs, and ventured to point out the relationship I believe it to bear to some of the well-known and remarkable compounds of carbon with nitrogen.

In concluding this lecture, I need simply remind the audience I have the honour to address that the practical value of scientific research is rarely apparent at first. Who could have suspected that the benzole discovered by the venerable philosopher whose name is so inseparably connected with this Institution, would have proved, in the able hands of Perkin and of Hofmann, the chief source of many of the exquisite dyes now largely manufactured in this country? Yet in this, as in a hundred of other instances, the small and apparently useless scientific seedling has gradually expanded into the strong tree, yielding its rich store of useful fruit. Let us hope that a similar future awaits some of the alcohols from flint which have been referred to this evening, and that, in pursuing our studies of the silicon analogues of the more complex carbon compounds, we may be led to appreciate more fully than we have hitherto done the admirable economy and harmony of Nature.

[J. E. R.]

Friday, May 23, 1873.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

WILLIAM SPOTTISWOODE, Esq. LL.D. M.A. Treas. R.S. Sec. R.I.

On Spectra of Polarized Light.

SOME apology is perhaps due to you on my part for proposing that you should come together for such elementary experiments as those which I have to offer you this evening, but the growing importance of the subject of polarization, both in general and in astronomical physics, and the increased instrumental means at our command for the study and the exhibition of the phenomena, all seem to indicate that an hour may be not unprofitably spent in trying to obtain a clearer insight into the fundamental parts of the subject.

The object which I propose on this occasion is to verify experimentally the explanation furnished by the wave theory of the colours produced by crystal plates when submitted to polarized light. Not because the wave theory or its conclusions need in themselves any verification, but because the line of argument ought to be continuous throughout,—not like an electric current which leaps from one part of a broken conductor to another. Each line, whether theoretical or experimental, should be complete and continuous from one end to another.

Having this object in view, I propose to reproduce, by way of memorandum, a few of the phenomena in question, so as to bring them and their analysis in as close juxtaposition as possible; and for this purpose I have arranged two electric lamps, each furnished with a complete polarizing apparatus, but the second having in addition a pair of dispersive prisms, forming, in fact, a spectroscope. In the first arrangement I would draw your particular attention to a

Nicol's prism or polarizer, superior in respect of size, and in the opinion of those best capable of judging, not inferior in quality to any hitherto constructed. We have, in fact, before us, first the pair of Nicols constructed by Mr. Ladd, which accompanied Professor Tyndall in his journey to the United States; secondly, a larger one made for him by Mr. Browning; and thirdly, the largest of all, by Messrs. Tisley and Spiller. And lest it should seem that in thus proceeding from large to larger we have been aiming merely at indefinite size, I may explain that my object has been always a strictly definite one, *viz.* to obtain a polarizer large enough to transmit the entire beam which issues from the lantern; in this I have now completely succeeded.

Now it is well known that if a plate of selenite sufficiently thin be placed between two such Nicol's prisms, or, more technically speaking, between a polarizer and analyzer, colour will be produced. And the question proposed is, What is the nature of that colour? is it simply a pure colour of the spectrum, or is it compound, and if so, what are its component parts? The answer given by the wave theory is in brief this: In its passage through the selenite plate the rays have been so separated in the direction of their vibrations and in the velocity of their transmission, that, when re-compounded by means of the analyzer, they have in some instances neutralized one another. If this be the case, the fact ought to be visible when the beam emerging from the analyzer is dispersed by the spectroscope; for then we have the rays of all the different colours ranged side by side, and if any be wanting, their absence will be shown by the appearance of a dark band in their place in the spectrum. But not only so; the spectrum ought also to give an account of the other phenomena exhibited by the selenite when the analyzer is turned round, *viz.* that when the angle of turning amounts to 45° all trace of colour disappears; and also that when the angle amounts to 90° colour reappears, not, however, the original colour, but one complementary to it.

You now see in the spectrum of the reddish light produced by the selenite a broad but dark band in the blue; when the analyzer is turned round the band becomes less and less dark, until when the angle of turning amounts to 45° it has entirely disappeared. At this stage each part of the spectrum has its own proportional intensity, and the whole produces the colourless image seen without the spectroscope. Lastly, as the turning of the analyzer is continued, a dark band appears in the red, the part of the spectrum complementary to that occupied by the first band; and the darkness is most complete when the turning amounts to 90° . Thus we have from the spectroscope a complete account of what has taken place to produce the original colour and its changes.

It is further well known that the colour produced by a selenite, or other crystal plate is dependent upon the thickness of the plate. And, in fact, if a series of plates be taken, giving different colours, their spectra are found to show bands arranged in different positions. The thinner plates show bands in the parts of the spectrum nearest

to the violet, where the waves are shorter, and consequently give rise to redder colours; while the thicker show bands nearer to the red, where the waves are longer, and consequently supply bluer tints.

When the thickness of the plate is continually increased, so that the colour produced has gone through the complete cycle of the spectrum, a further increase of thickness causes a reproduction of the colours in the same order; but it will be noticed that at each recurrence of the cycle the tints become paler, until when a number of cycles have been performed, and the thickness of the plate is considerable, all trace of colour is lost. Let us now take a series of plates, the first two of which, as you see, give colours; with the others which are successively of greater thickness the tints are so feeble that they can scarcely be distinguished. The spectrum of the first shows a single band; that of the second, two; showing that the second series of tints is not identical with the first, but that it is produced by the extinction of two colours from the components of white light. The spectra of the others show series of bands more and more numerous in proportion to the thickness of the plate, an array which may be increased indefinitely. The total light, then, of which the spectrum is deprived by the thicker plates is taken from a greater number of its parts; or, in other words, the light which still remains is distributed more and more evenly over the spectrum; and in the same proportion the sum total of it approaches more and more nearly to white light.

These experiments were made more than thirty years ago by the French philosophers, MM. Foucault and Fizeau.

If instead of selenite, Iceland spar, or other ordinary crystals, we use plates of quartz cut perpendicularly to the axis, and turn the analyzer round as before, the light, instead of exhibiting only one colour and its complementary with an intermediate stage in which colour is absent, changes continuously in tint; and the order of the colour depends partly upon the direction in which the analyzer is turned, and partly upon the character of the crystal, *i. e.* whether it is right-handed or left-handed. If we examine the spectrum in this case we find that the dark band never disappears, but marches from one end of the spectrum to another, or *vice versa*, precisely in such a direction as to give rise to the tints seen by direct projection.

The kind of polarization effected by the quartz plates is called circular, while that effected by the other class of crystals is called plane, on account of the form of the vibrations executed by the molecules of æther; and this leads us to examine a little more closely the nature of the polarization of different parts of these spectra of polarized light.

Now, two things are clear: first, that if light be plane-polarized, that is, if all the vibrations throughout the entire ray are rectilinear and in one plane, they must in all their bearings have reference to a particular direction in space, so that they will be differently affected by different positions of the analyzer. Secondly, that if the vibrations be circular, they will be affected in precisely the same way (whatever

that may be) in all positions of the analyzer. This statement merely recapitulates a fundamental point in polarization. In fact, plane-polarized light is alternately transmitted and extinguished by the analyzer as it is turned through 90° ; while circularly-polarized light remains to all appearance unchanged. And if we examine carefully the spectrum of light which has passed through a selenite, or other ordinary crystal, we shall find that, commencing with two consecutive bands in position, the parts occupied by the bands and those midway between them are plane-polarized, for they become alternately dark and bright; while the intermediate parts, *i. e.* the parts at one-fourth of the distance from one band to the next remain permanently bright. These are, in fact, circularly polarized. But it would be incorrect to conclude from this experiment alone that such is really the case, because the same appearance would be seen if those parts were unpolarized, *i. e.* in the condition of ordinary lights. And on such a supposition we should conclude with equal justice that the parts on either side of the parts last mentioned (*e. g.* the parts separated by eighth parts of the interval between two bands) were partially polarized. But there is an instrument of very simple construction, called a "quarter-undulation plate," a plate usually of mica, whose thickness is an odd multiple of a quarter of a wave length, which enables us to discriminate between light unpolarized and circularly polarized. The exact mechanical effect produced upon the ray could hardly be explained in detail within our present limits of time; but suffice it for the present to say that when placed in a proper position, the plate transforms plane into circular and circular into plane polarization. That being so, the parts which were originally banded ought to remain bright, and those which originally remained bright ought to become banded during the rotation of the analyzer. The general effect to the eye will consequently be a general shifting of the bands through one-fourth of the space which separates each pair.

Circular polarization, like circular motion generally, may of course be of two kinds, which differ only in the direction of the motion. And, in fact, to convert the circular polarization produced by this plate from one of these kinds to the other (say from right-handed to left-handed, or *vice versa*), we have only to turn the plate round through 90° . Conversely right-handed circular polarization will be changed by the plate into plane-polarization in one direction, while left-handed will be changed into plane at right angles to the first. Hence, if the plate be turned round through 90° we shall see that the bands are shifted in a direction opposite to that in which they were moved at first. In this therefore we have evidence not only that the polarization immediately on either side of a band is circular; but also that that immediately on the one side is right-handed, while that immediately on the other is left-handed.

If time permitted, I might enter still further into detail, and show that the polarization between the plane and the circular is elliptical, and even the positions of the longer and shorter axes and the direction

of motion in each case. But sufficient has, perhaps, been said for our present purpose.

Before proceeding to the more varied forms of spectral bands, which I hope presently to bring under your notice, I should like to ask your attention for a few minutes to the peculiar phenomena exhibited when two plates of selenite giving complementary colours are used. The appearance of the spectrum varies with the relative position of the plates. If they are similarly placed, that is as if they were one plate of crystal, they will behave as a single plate, whose thickness is the sum of the thicknesses of each, and will produce double the number of bands which one alone would give; and when the analyzer is turned, the bands will disappear and re-appear in their complementary positions, as usual in the case of plane-polarization. If one of them be turned round through 45° , a single band will be seen at a particular position in the spectrum. This breaks into two, which recede from one another towards the red and violet ends respectively, or advance towards one another according to the direction in which the analyzer is turned. If the plate be turned through 45° in the opposite direction, the effects will be reversed. The darkness of the bands is, however, not equally complete during their whole passage. Lastly, if one of the plates be turned through 90° , no bands will be seen, and the spectrum will be alternately bright and dark, as if no plates were used, except only that the polarization is itself turned through 90° .

If a wedge shaped crystal be used, the bands, instead of being straight, will cross the spectrum diagonally, the direction of the diagonal (dexter or sinister) being determined by the position of the thicker end of the wedge. If two similar wedges be used with their thickest ends together, they will act as a wedge whose angle and whose thickness is double of the first. If they be placed in the reverse position they will act as a flat plate, and the bands will again cross the spectrum in straight lines at right angles to its length.

If a concave plate be used the bands will dispose themselves in a fanlike arrangement, their divergence depending upon the distance of the slit from the centre of concavity.

If two quartz wedges, one of which has the optic axis parallel to the edge of the refractory angle, and the other perpendicular to it, but in one of the planes containing the angle (Babinet's Compensator), the appearances of the bands are very various.

The diagonal bands, beside sometimes doubling themselves as with ordinary wedges, sometimes combine so as to form longitudinal (instead of transverse) bands; and sometimes cross one another so as to form a diaper pattern with bright compartments in a dark framework, and *vice versa*, according to the position of the plates.

The effects of different dispositions of the interposed crystals might be varied indefinitely; but enough has, perhaps been said to show the delicacy of the method of spectrum analysis as applied to the examination of polarized light.

[W. S.]

Friday, June 6, 1873.

SIR HENRY HOLLAND, Bart. M.D. D.C.L. F.R.S. President,
in the Chair.

PROFESSOR ODLING, M.A. F.R.S.

On Evaporation and Diffusion.

OF the circumstances on which the rate of evaporation of the same volatile substance chiefly depends, one very influential circumstance, namely, the nature of the atmosphere into which the vapour proceeds and distributes itself, does not appear to have been made the subject of careful examination. There is, however, one familiar experiment on the subject; and it consists in passing up a little ether into two equal volumes, one of hydrogen and the other of air, contained in similar cylinders standing over water. Evaporation of the ether takes place in both cases; though far more rapidly into the hydrogen than into the air, as shown by the far more rapid expansion of the hydrogenous than of the aerial space, from the addition to it of the ether-vapour. This experiment is usually cited in illustration of the greater rapidity at which ether-vapour diffuses itself into an atmosphere of light hydrogen than into an atmosphere of comparatively heavy air. It is doubtful, however, whether the explanation in this precise form is strictly correct, the diffusive mobility of any gas or vapour being a property altogether special to itself, irrespective of extraneous conditions. Thus, in a particular experiment, Mr. Graham found that while the quantity of hydrogen which in one minute of time passed through a graphite plate into a vacuum was 1·289 c. c., the quantity of hydrogen which in the same time passed through the same graphite plate into the surrounding air was 1·243 c. c., or almost exactly the same.

A novel experiment on the influence due to the nature of the contiguous atmosphere upon the rapidity of the process of evaporation, consists in introducing into each of two similar tall cylinder bottles a sealed glass bulb containing a little iodine. The one cylinder being filled with hydrogen, and the other with air, and each having suspended from its mouth a piece of starched paper or cloth, the bulbs are then broken by concussion of the containing cylinders. But, in this case, the test paper or cloth suspended in the cylinder of air becomes affected by the iodine considerably before that suspended in the cylinder of hydrogen; or, contrary to what happens with ether, the iodine *appears* to volatilize more quickly in the comparatively heavy air than in the much lighter hydrogen. Similarly, if some weak aqueous ammonia contained in a sealed glass bulb be set free in

a tall bottle of hydrogen, and also in a tall bottle of air, a piece of turmeric paper suspended from the stopper of each bottle becomes affected by the ammonia vapour more quickly in the bottle of air than in the bottle of hydrogen.

Water may be taken as the type of a volatile substance, and the nature of the process of evaporation be conveniently studied in relation thereto. Now, in a hermetically-closed vessel exhausted of air, but partly filled with water, the matter of the water exists in two states—a portion of it in the liquid state, and another portion in the aerial, or vaporous, or evaporated state; and, with excess of liquid water present, the quantity of vaporous water that can exist in an otherwise vacuous space, or the density of the vapour filling the space, is found to vary solely with the temperature. Thus 100 cubic inches of space will contain at 58°C ., 3 grains of vaporous water; at 100°C ., 15 grains; at 144°C ., 58 grains, and so on; or the densities of the vapour of water at these different temperatures are as the numbers, 3, 15, and 58, respectively. Now, the quantity of water-vapour that can exist at any particular temperature in a volume of otherwise vacuous space, is almost identical—it used to be considered absolutely identical,—with the quantity of vapour that can exist in the same volume of space already occupied by air. In other words, a cubic inch of water-vapour, and a cubic inch of air saturated with water-vapour, contain the same weight of the matter of water. Hence it is found that with continuous increase of temperature, a greater and greater quantity of liquid water ceases to be liquid and becomes vaporous, or is, in other words, evaporated into the adjoining space, whether vacuous or aerial; and conversely with decrease of temperature, a greater and greater quantity of vaporous water ceases to be vaporous, and is deposited in the liquid state. Thus, upon cooling a globe of transparent warm moist air, it is at once filled with an opaque mist, which, left to itself, soon becomes deposited in the form of drops; but which may be readily made to disappear or re-vaporize by gently heating the globe. The deposition of dew on cold surfaces brought into a warm moist room is familiar to all.

The tension or spring of water-vapour varies with the quantity of vapour filling the space—that is, with the density of the vapour, and consequently with its temperature. Thus the tension is equal at 15°C ., to a pressure of 13 millimètres of mercury; at 60°C ., to a pressure of 149 millimètres; at 100°C ., to a pressure of 760 millimètres; at 144°C ., to a pressure of 3040 millimètres. At the temperature of 100°C ., the tension of the vapour of water being equal to a pressure of 760 millimètres of mercury, balances the tension or pressure of the atmosphere, as measured by the height of the barometric column. Hence on continuing to heat water already at the temperature of 100° , it boils, or is converted into vapour, having a tension equal to that of the atmosphere. And so with a less or greater external pressure, water boils at a lower or higher temperature—in each case at the particular temperature whereat the elastic force of the water-vapour

balances the particular external pressure. Under a pressure of 149 millimètres, for instance, water boils at 60° C.; under a pressure of 3040 millimètres, it boils at 144° C. The occurrence, then, of ebullition at some particular point of temperature may be viewed as a mere accident of the process of evaporation—a more and more rapid evaporation, with production of vapour of higher and higher density and elasticity, proceeding continuously with the continuous increase of temperature, although, indeed, at a far more rapid rate than the rate of increase of temperature.

In the conversion of liquid water into water-vapour, heat is absorbed. It was at one time considered that the quantity of heat absorbed was independent of the temperature and correlative tension of the vapour yielded, and that it varied only with the quantity yielded. It was held, for example, that in the conversion, say, of a gramme of liquid water into a gramme of water-vapour—whether of tenuous vapour at a low temperature, or of dense vapour at a high temperature—the same quantity of heat was absorbed. This rule, though now known to be only approximatively true, is nevertheless sufficiently true to allow of the amount of cold, or absorption of heat, resulting from any evaporation, being taken as an indication or measure of the amount of that evaporation. The depression of temperature caused by the evaporation of water, is familiarly shown in the use of the wet-bulb hygrometer. This instrument consisting simply of a couple of thermometers, one of which has its bulb kept continuously moist, the difference in way of deficit between the temperature manifested by this wet-bulb thermometer and the temperature manifested by the other thermometer, is a measure of the amount of water evaporating from the surface of the moistened bulb.

What is true of liquid water and of water-vapour is true, in principle, of other volatile liquids and of their several vapours. At any given temperature some of these bodies volatilize much more rapidly, others of them much less rapidly, than one another, and than water; and in the process of their evaporation some of them absorb a much greater amount of heat than others, though for the same weight of vapour formed no one of them is known to absorb so large an amount of heat as water. Disulphide of carbon, ether, and alcohol, are familiar examples of bodies more volatile than water; aniline, mercury, and molten silver, of bodies less volatile. It is well known that water when required pure is distilled—that is to say, it is first vaporized by heat and then re-liquefied by cold; and silver when required absolutely pure is sometimes submitted to the same process of distillation. Evaporation is, moreover, a property not only of liquid, but also of solid bodies, as of sal-ammoniac, iodine, camphor, ice and snow, solid carbonic acid, &c. Many of the phenomena of evaporation can be illustrated more conveniently with other volatile substances than with water. Thus the cooling produced by evaporation may be strikingly illustrated by means of ether, and still more strikingly by means of some liquefied gas, as liquefied sulphurous or nitrous oxide.

The necessary influence of some conditions on the rate of evaporation is obvious. Evaporation being a direct result of the absorption of heat, and the higher the temperature the greater the quantity of vapour capable of existing in a given space, it is found that at higher and higher temperatures water evaporates or dries up more and more rapidly, in proportion approximatively to the increasing density of the vapour at higher and higher temperatures. Wet linen, for example, is habitually dried by being hung before the fire or placed in heated chambers or ovens.

Similarly with regard to the influence of the extent of liquid surface on the rate of evaporation, it is found that the evaporation of a given weight of liquid water takes place more rapidly when the water is spread out in a wide dish than when it is contained in a narrow tube, in proportion to the greater extent of surface from which the evaporation can take place in the one case than in the other. Thus, while half a pint of water in a tumbler will remain for an almost indefinite time without becoming dried up, half a pint of water absorbed in a thick towel exposing on its two sides more than a dozen square feet of surface, will become dried up in the course of twenty-four hours.

Again, the influence exerted by the greater or less dryness of the adjacent space, whether or not aerial, upon the evaporation of water is obvious. Into a space already saturated with vapour no further evaporation whatever can take place; and other conditions being alike, the drier the space the greater the amount of evaporation that can take place with it, and the more rapid the process of evaporation. In the laboratory, moist substances are made dry by allowing the water from them to evaporate into spaces kept artificially dry by means of desiccating agents, such as oil of vitriol, quicklime, chloride of calcium, &c., which absorb the water-vapour from the space as fast as it is produced therein. Moreover, evaporation proceeding into any space, vacuum or aerial, until the space is saturated with water-vapour, and more rapidly in proportion to the removal from saturation of the space, it is obvious that, other conditions being equal, evaporation proceeds more rapidly into a large space requiring for its saturation a considerable weight of water-vapour than into a small space capable of being saturated by a minute quantity of the vapour.

The influence of the extent of aerial space into which a vapour can distribute itself upon the rate of formation of the vapour, leads to a consideration of the effect of the movement of the contiguous air upon the rate of evaporation from a given surface. With an absolutely quiescent atmosphere, the layer of atmosphere in immediate contact with the surface of evaporating liquid must become quickly saturated with vapour; and but for some spontaneous means of removal of the vapour itself, or of the air saturated with it, from the surface of the liquid, all further evaporation would be arrested. The nature of these spontaneous means of removal will be considered

presently ; but the influence of the artificial removal of the more or less saturated air from the surface of the evaporating liquid can be easily manifested. Thus on allowing a strong current of air to play upon a surface of ether contained in a thin glass vessel standing on a stratum of water, the stratum of water becomes quickly frozen by reason of the heat abstracted from it, in the rapid production of ether-vapour which takes place in the current of air. For whereas with the ether in the vessel left to itself, the interior of the vessel soon becomes saturated with ether-vapour, and further evaporation with correlative cooling effect is almost arrested ; with a current of air blown on to the surface of the ether, the liquid ether is in continuous contact with a fresh unsaturated atmosphere, into which it continues to evaporate with rapidity.

In connection with the above influences, it is observable that the evaporation of water from growing plants is favoured by the three conditions of extent of leaf surface, movement of the more or less dry atmosphere, and heat of the summer sun. An early and very striking experiment on the extent of this evaporation was made by Dr. Stephen Hales in 1724, and is recorded in his 'Vegetable Statics.' He found that with a healthy full-grown sunflower more than a yard high, planted when young in a suitable pot, the evaporation from the plant itself amounted on the average to 20 ounces in a twelve hours' day, the maximum quantity being 30 ounces. Some very interesting and exact modern experiments on this subject were conducted in 1850 by Mr. Lawes at Rothamstead. As an example of the results obtained, he found that a plant of barley, during a period of 172 days' growth, in which it acquired 419 grains of dry organic, and 46 grains of dry mineral matter, evaporated not less than 120,000 grains, or upwards of 17 lbs. of water ; so that for every grain of dry matter, organic and mineral, fixed by the plant during its period of growth, 257 grains of water were absorbed and evaporated.

A most important condition affecting the rate of evaporation is the pressure on the surface of the volatile substance. Into a vacuum indeed, where there is no pressure, evaporation is practically instantaneous. Thus on letting up a little water, alcohol, or ether into the vacuum of a barometer, the mercury is at once depressed to the maximum extent producible by the tension of the particular vapour at the particular temperature. Again, on breaking a sealed bulb of iodine, within and at the lower end of a long scaled vacuum tube, a piece of starch-paper at the upper end of the tube is almost immediately affected by the iodine vapour. Further, the cooling consequent on the rapid evaporation of ether, ammonia, &c., into a vacuum, is taken advantage of in the construction of several well-known freezing machines. Again, in Leslie's celebrated experiment, the evaporation even of water into a vacuum space, from which the water-vapour is removed by some desiccant as fast as produced, takes place with such rapidity and correlative absorption of heat, as to effect the freezing of the residual water from which the evaporation is proceeding. The same

result is effected in Wollaston's cryophorus, the water-vapour in this case not being absorbed by oil of vitriol or other desiccant, but being simply condensed by cold applied to the other and distant bulb of the twice bent vacuum tube. Moreover, it was long ago shown by Daniel that evaporation of water into the same dry atmosphere takes place at a rate inversely proportioned to the pressure of the atmosphere. Thus in a particular set of experiments, the pressures of the air being 30.4, 15.2, and 7.6 inches of mercury, the quantities of water evaporated in half an hour were found to be 1.24, 2.97, and 5.68 grains respectively.

That the nature of the atmosphere into which a vapour can distribute itself has an important influence on the rate of formation of the vapour may be manifested by several experiments, in addition to those shown at the beginning of the lecture. Thus with a couple of thin glasses standing on a stratum of water, and containing each some rectified wood-spirit, if the one portion of spirit be blown upon by a strong current of hydrogen, and the other portion by a strong current of air, the stratum of water underlying the glass of spirit blown upon by the hydrogen, will alone become frozen, by reason of the excessive vaporization of, and heat-absorption by, the spirit in contact with the atmosphere of hydrogen. Again, a series of experiments has recently been made by the speaker on the relative rates of evaporation of water into limited atmospheres of hydrogen, air, and carbonic acid respectively, alike kept dry by contact with a large surface of oil of vitriol. In these experiments, the evaporation was found to take place most rapidly in hydrogen, and least rapidly in carbonic acid; and as a mean of seven tolerably concordant results, the ratio of the rate of evaporation in hydrogen to the rate of evaporation in air, under the particular conditions of the experiment, was found to be as 2.68 : 1.

The influence of the particular contiguous atmosphere on the rate of evaporation of any particular liquid may be, and probably is, of a very complex nature. There are, however, two easily intelligible ways in which the particular atmosphere may act by virtue of its specific gravity. Thus a lighter or heavier gas or vapour ascends or descends bodily through another at a rate proportionate to the difference in their specific gravities, a very slight difference sufficing to bring about an upward or downward current of considerable activity. This upward or downward movement is well shown by introducing first heavy ether-vapour, and then light coal-gas, through a lateral opening made at about the middle of the length of a tall somewhat wide perpendicular glass tube, open at both ends; when it will be found that the ether-vapour, descending by reason of its heaviness, can only be inflamed at the bottom of the tube, while the coal-gas, ascending by reason of its lightness, can only be inflamed at the top. Now, the specific gravities of hydrogen, aqueous vapour, and air at the same temperature, being to one another as the numbers 1, 9, and 14.5 respectively, it is obvious that whereas hydrogen saturated with water-vapour is heavier than dry hydrogen, air saturated

with water-vapour is lighter than dry air. Accordingly, with a surface of water exposed to an atmosphere of originally dry hydrogen, the hydrogen in actual contact with the water will not, by becoming moist, acquire a tendency to rise up through the dry hydrogen, and so be removed from the surface of the liquid; whereas, with a surface of water exposed to an atmosphere of originally dry air, the air in actual contact with the water will, by becoming moist, acquire a tendency to rise up through the dry air, and so become removed from the surface of the liquid. And having regard to this influence alone, water when occupying an inferior position, should evaporate more rapidly into air than into hydrogen. It must be borne in mind that any given volume of moist air or gas is the sum of the volume of its constituent water-vapour, and of the volume of its constituent dry air or gas; and that the tension of the moist air or gas is the sum of the tension of its constituent water-vapour, and of the tension of its constituent dry air or gas, actually or virtually expanded by the addition to it of a certain volume of water-vapour. So that with water boiling in a deep open vessel, there may exist in close proximity to each other, almost pure water-vapour, different mixtures of water-vapour and air, and comparatively dry air, all having alike a tension of 760 millimètres of mercury.

But independently of their bodily movements in the form of currents, gases and vapours distribute themselves among one another by a proper molecular movement of diffusion—the relative diffusive mobilities of different gases or vapours being inversely as the square roots of their several specific gravities. Accordingly, with equal surfaces of water exposed respectively to an atmosphere of hydrogen and to an atmosphere of air, the vapour produced from the surface of the water is interpenetrated and distributed through the contiguous space with greater rapidity by the highly-diffusive hydrogen than by the feebly-diffusive air, in proportion to their relative diffusion-velocities, 3·8 and 1·0 respectively. And it is, doubtless, to the more rapid diffusion of hydrogen than of air into the vapour as formed, and the consequent more rapid supply to the liquid of an unsaturated atmosphere into which it can evaporate, that the more rapid evaporation of water, ether, and wood-spirit into an atmosphere of hydrogen than into an atmosphere of air, as in the experiments, for instance, already shown and described, is substantially due.

[W. O.]

Friday, April 17, 1874.

THE DUKE OF NORTHUMBERLAND, D.C.L. President, in the Chair.

WILLIAM SPOTTISWOODE, Esq. LL.D. Treas.R.S. Sec.R.I.

On Combinations of Colour by means of Polarized Light.

It is well known that if a beam of polarized light, which has passed through a plate of crystal, be analyzed with a double-image prism, two images will be seen tinted with complementary colours. The fact that the colours are complementary may be established by causing the images to overlap, when the part of the field of view common to both will be found to be white. And further, if the plate be of quartz cut perpendicularly to the axis, the images will change colour by a continuous sequence of tints when either polarizer or analyzer is turned continuously round. The colours so seen are, however, not simple colours of the spectrum, but mixed or residual tints, *viz.* the mixture of all those which remain when one or more have been extinguished. This is a direct deduction from the principles of the wave theory of light; but it was also practically demonstrated in some experiments which I had the honour of laying before the Institution last year. And, in fact, if we use a quartz plate of suitable thickness, and examine the spectrum of either of the images formed by the analyzer, we shall find it crossed with a single dark band which moves along the spectrum in one direction or the other, according to the sense in which either polarizer or analyzer is turned.

This principle enables us to make use of polarized light for investigating the subject of complementary colours. For if we form the spectra of the two complementary images, we shall find in general that the dark band occupies one position in the ordinary, and another in the extraordinary image. But since the two images are complementary to one another, and the part extinguished in each is complementary to the part which remains, it follows that the part extinguished in one is the complementary of the part extinguished in the other. That is to say, the bands in the two spectra will always mark out two complementary portions of the spectrum. It must, however, be borne in mind that the bands are not sharply defined like the Fraunhofer lines in the solar spectrum, but they are bands with a core of minimum or zero illumination shading off gradually on either side; so rapidly, however, that at a short distance from the core the adjoining colours

appear in their full natural intensity. This being so, the tint suppressed in any band will be a compound of portions of all the colours comprised within the visible limits of the band. Of the colour corresponding to the core the whole will be suppressed, but of those on each side only portions, smaller and smaller as we recede from the core. And if we use the term "colour suppressed" in this sense, the pairs of colours determined by this method will be found to agree in the main with those given by Helmholtz as the result of the superposition of two spectra at right angles to one another, *viz.* : —

Yellow-green,
Yellow,
Orange,
Red,

Violet;
Indigo-blue;
Cyanic-blue;
Green-blue.

It will be noticed that, when one band arrives at the green moving in the direction of the red, the other or complementary band is just disappearing in the red; but at the same time another band is beginning to appear in the violet. We cannot therefore say that the green has for its complementary the red rather than the violet; the complementary in question is in fact a mixture of the two, a mixture which, when taken alone, is a reddish purple. This result agrees with the conclusion derived by Helmholtz from his own experiments.

Starting from the principle of these interference bands of polarized light, it occurred to me that if two or more such bands could be formed, and could be made to move independently and at pleasure in either direction along the spectrum, we should have the means of at once determining, and exhibiting, at all events the tints complementary to a combination of two or more bands chosen at will from the spectrum. And pursuing this subject further, I found not only that this is possible, but succeeded, by a combination of double-image prisms, actually to form in the field of view the tints complementary to the above-mentioned complementaries; in other words, tints which represent the mixture of the two portions of the spectrum suppressed in the bands. For this purpose I have used, instead of the ordinary polarizing apparatus, the following arrangement, reckoned from the source of light towards the eye or screen. First, a Nicol's prism N as polarizer, then a quartz plate Q, next a double-image prism P; after that a second quartz plate Q₁, and finally a second double-image prism P₁. By this means four images are formed in the field of view—say, O O, O E, E O, E E, whereof O O, O E, occupy the positions of the two images formed by P alone; and O O, E O, the positions of those formed by P₁ alone. If for a moment we remove the second quartz plate, the arrangement above described will furnish some interesting experimental illustrations of the conclusions stated by Helmholtz—*viz.* that the low tint colours (*couleurs dégradées*) such as russet, brown, olive-green, peacock-blue, are the result of low illumination. He mentions that he obtained these effects by diminishing the intensity of the light in the colours to be examined, and by, at the same time, maintaining

a brilliantly illuminated patch in an adjoining part of the field of view. In accordance with what was said before, in the case where no quartz plate was used, it appears that by turning the prism P_1 round, we have the power of diminishing to any extent we please the intensity of the light in one pair of the complementary images, and at the same time increasing that in the other pair. We therefore have an equivalent of the conditions of Helmholtz's experiments. The conclusions were verified by throwing on the screen the spectra of two similarly tinted images, one highly, the other feebly illuminated, when it was found that the band occupied the same position in both spectra.

If a second quartz plate Q_1 be re-inserted between the prisms P, P_1 , there will be 15 combinations of colour to consider, *viz.* 4 single images, 6 overlaps of two, 4 overlaps of three, and 1 overlap of all four images.

The tints of the four single images will now be those due to the formation of two bands in spectrum of each, *viz.* one due to the combination $Q P$, the other to the combination $Q_1 P_1$. It will therefore be convenient in this case to designate their tints by the lines of letters representing the bands; thus, $B + A, B + A', B' + A, B' + A'$; in which it is to be understood that A, A' represent the pair of complementary bands formed by $Q P$, and B, B' the pair extinguished by $Q_1 P_1$.

The following is an arrangement of the images formed by P and P_1 , together with the tints corresponding to the bands in each:--

$$\begin{array}{ccc}
 & O O & \\
 & B + A & \\
 E O & & O E \\
 B' + A & & B' + A' \\
 & E E & \\
 & B + A' &
 \end{array}$$

OO represents the ordinary image of P and P_1 ; OE the ordinary image of P_1 and the extraordinary of P ; &c. It is to be observed that $B + A, B' + A'$, occupy the positions of the two images formed by P alone; and $B + A, B' + A$, those of the images formed by P_1 alone. And it would at first sight appear that the colours suppressed in the first-mentioned images would be $B + A, B + A'$; but it must be remembered that the vibrations in the two images O, E , formed by P are at right angles to one another, and consequently the instrumental combination $Q_1 P_1$ will in forming its ordinary image of A suppress the colour B , but in the ordinary image of A' it will suppress its complementary B' . A similar remark applies to the other pair of images.

The effect of the combinations $Q_1 P_1$ is to divide the images OO, OE , respectively into two parts, in one of which the colour B , in the other B' , is suppressed. Hence the overlap of $B + A$ and $B' + A$, will reproduce the original colour minus only the complementaries B, B' . This overlap may consequently be formularized thus,

$$B + A + B' + A = B + B' + 2 A.$$

Similarly we may write

$$B + A' + B' + A' = B + B' + 2 A'.$$

In other words, these two overlaps will be tinted with the colours A, A' . This may be verified by taking away the combination $Q_1 P_1$. And further, since the vibrations in the images $B + A, B' + A$, are at right angles to one another (as likewise are those in $B + A', B' + A'$), it follows that when the polarizer N is turned round and the images change colour, the complementary character of the overlaps in question will always be maintained.

The same will be the case with the overlaps $B + A, B + A'$; and $B' + A, B' + A'$. But in order to verify this in the same way as in the former case, *viz.* by taking away the combination $Q P$, it must be borne in mind that the original plane of polarization must coincide with that of one of the images produced by $Q_1 P_1$. And it may be further noticed that if the original plane of polarization be altered by turning the Nicol N alone, the angle between the principal planes of P and P_1 will remain the same; and consequently the overlap in question will continue of the same colour whatever be the position of N .

Lastly, as regards the overlaps of $B + A$ and $B' + A'$, and of $B' + A$ and $B + A'$. It is clear that in both cases the images will have been deprived of the two pairs of complementary colours A, A', B, B' ; and therefore if the suppressed colours were all of the same intensity the overlaps would be uniformly white or grey. But as this is not the case, the parts in question will in general be tinted with the colours complementary to the feeblest of those suppressed. In fact, in the images

$$B + A \text{ and } B' + A',$$

if A be a feeble colour, A' will in general be strong, and excepting when the reverse is the case with B and B' , the tint of $B + A$ will depend mainly on that produced by $Q P$, while that of $B' + A'$ will depend mainly on that produced by $Q_1 P_1$. Again, if in the same images, B approaches to A' , then will B' approach A , and the two images will approach the same tint; while on the other hand, under the same circumstances the images

$$B + A' \text{ and } B' + A$$

will approach to complementary tints. In proportion as the common colour of the two first-mentioned images approaches to a grey, so will the overlap of the two last mentioned approach to white. In other cases the two overlaps in question will be of complementary tints.

We might apply the same train of reasoning to the triple overlaps, but the main interest of these parts of the figure consists in this, that each of the triple overlaps is complementary to the fourth single image not comprised in it; *e.g.* $B + A$ is complementary to $B' + A + B + A' + B' + A'$; and similarly for the others. This follows from the obvious fact that the quadruple overlap of all four

single images is necessarily white. But the colours suppressed in each single image are together complementary to the colour of the image. Hence the colour of any triple overlap is the same to the eye as the mixture of the two colours suppressed in the outstanding single image. But since by turning the Nicol N we can displace the two bands in any way we please, and also by turning P_1 we can displace one of them in any way, we have the power of suppressing any two portions of the spectrum at will, and consequently of exhibiting to the eye the result of the combination of any two such portions.

A further step in the combination of colour may be made by using a third quartz Q_2 , and a third double-image prism P_2 , which will give rise to eight images; and using symbols similar to those used before, we may represent the tints suppressed by $Q_2 P_2$ by the letters $C C'$. The number of tints suppressed in each image is consequently three; and by seeking out the compartments which give the complementaries of each of the eight images, we shall have the representations of the three tints suppressed. It is hardly necessary to point out that by causing different parts $Q P$, $Q_1 P_1$, $Q_2 P_2$, of the instrument to rotate, we can suppress any three tints at will. The formulæ for the eight images will be

$C + B + A$	or	OOO
$C + B' + A'$	„	OOE
$C' + B' + A$	„	OEO
$C' + B + A'$	„	OOE
$C' + B + A$	„	EOO
$C' + B' + A'$	„	EOE
$C + B' + A$	„	EEO
$C + B + A'$	„	EEE

The number of combinations of tint as given by the compartments of the complete figure is as follows:—

$\frac{8}{1}$	=	8 single
$\frac{8.7}{1.2}$	=	28 double
$\frac{8.7.6}{1.2.3}$	=	56 triple
$\frac{8.7.6.5}{1.2.3.4}$	=	70 quadruple
$\frac{8.7.6}{1.2.3}$	=	56 quintuple
$\frac{8.7}{1.2}$	=	28 sextuple
$\frac{8}{1}$	=	8 septuple
1	=	1 octuple

or 255 in all. It is perhaps unnecessary to follow these combinations out in detail, especially as the most interesting feature

consists in the fact that the subjoined pairs are complementary to one another, viz. :—

OOO C + B + A	EOE C' + B' + A'
EOO C' + B + A	OOE C + B' + A'
EEO C + B' + A	OEE C' + B + A'
EEE C + B + A'	OEO C' + B' + A

Having this table in view, the application of the figure to the visible representation of the mixture of colours is simpler in this case than in that of four images; for to each single image corresponds as complementary another single image, and we can at once read off the results required without seeking any overlaps.

When the double-image prisms are so arranged that the separations due to P , P_1 , P_2 , are directed parallel to the sides of an equilateral triangle respectively, it is not difficult to read off the images in pairs. The scheme of images may then be disposed as follows, viz. :

	OEO	OOO	
EEO	EOO	OEE	OOE
	EEE	OEO	

And the pairs will be read off two horizontally and two vertically, by taking alternate images in each horizontal and in each vertical row, thus :—

OOO,	FOE;
EOO,	OEE;
EEO,	OEE;
EEE,	OEO.

[W. S.]

Friday, April 24, 1874.

GEORGE BUSK, Esq. F.R.S. Treasurer and Vice-President,
in the Chair.

CHARLES WATKINS MERRIFIELD, Esq. F.R.S.

On Sea Waves.

THE speaker, in beginning his discourse, pointed out the special importance, in understanding the subject, of knowing that the advance of a wave is neither necessarily nor generally accompanied by any corresponding advance of the water itself. There are many other forms of motion in which this advance of form only occurs; and he exhibited large models of screws, pointing out that when the barrel on which the screw is cut is simply turned round without advancing, the screw-thread appears to advance like a series of waves; but that when the screw works in a nut, so that the screw advances, then the screw-thread remains apparently at rest. In the same way, in sea waves which appear to advance rapidly the water has no sensible motion of advance, while in the series of waves often seen below a bridge or shoal in a rapid river the water does advance, and the waves stand still.

What really constitutes a wave is that each particle of water shall go through the same little dance of its own, while the successive particles "take up the dance" in regular order. There will then be a wave or series of waves, whether there be any general movement or current in the water or not.

As the motion of a troubled sea is too complex to be understood without first considering the simpler forms of wave-motion, the speaker selected for illustration the simple succession of waves called "swell," or smooth ground-sea of deep water. This, as is well known, consists of a series of long unbroken ridges of water, apparently moving with considerable speed and force; yet, what the particles of water are actually doing is simply going round and round in circles in vertical planes; these planes being at right angles to the lines of the ridges, and the diameters of the circles being the height of the wave from valley to crest. There is no appreciable advance of the water; the advance of the wave being due to the particles taking up the dance in regular succession. If a disk or circle be rolled along the foot of a wall, a nail sticking out from it anywhere between its centre and its edge would trace on the wall the same curves (only upside down) as

the profiles of the wave. A screw-thread drawn in suitable perspective also gives the same curves.

After giving this general notion of the sea wave, Mr. Merrifield pointed out its internal mechanical structure, showing that it consists of a series of undulating stratified layers (forming horizontal planes when the water is still), which undergo no mixing with one another. In the same way the water may be also ideally separated into vertical columns, which again do not mix, but only sway to and fro like stalks of barley when the wind sweeps over the field of corn. Only in the sea waves the columns lengthen as the wave crest approaches and shorten after it has passed away, always leaning towards the crest of the wave. The swell or ground-sea of deep water thus simply heaves the mass of water without stirring or mixing it, and without any general motion of advance, notwithstanding the apparent rapid motion of the waves,

In this absolute form the kind of wave described is perhaps rather the limiting condition which the waves tend to assume when left to the action of gravity alone than a state of things absolutely realized. Still, the departure from it is much smaller than might be supposed; and the apparent confusion of motion, when once the wind ceases, is rather due to several systems of swell, of different dimensions, existing at the same time and place, than to any essential difference in the character of the motion. After some details respecting the combination of waves and their height and length, the discourse was concluded with some remarks on waves of shallow water, and on the formation of waves in a rising storm. The illustrations consisted of diagrams and models.

Friday, January 15, 1875.

GEORGE BUSK, Esq. F.R.S. Treasurer and Vice-President, in
the Chair.

PROFESSOR TYNDALL, D.C.L. LL.D. F.R.S. M.R.I.

On Acoustic Reversibility.

ON the 21st and 22nd of June, 1822, a Commission appointed by the Bureau of Longitudes of France executed a celebrated series of experiments on the velocity of sound. Two stations had been chosen, the one at Villejuif, the other at Montlhéry, both lying south of Paris, and 11·6 miles distant from each other. Prony, Mathieu, and Arago were the observers at Villejuif, while Humboldt, Bouvard, and Gay-Lussac were at Montlhéry. Guns, charged sometimes with 2 lb. and sometimes with 3 lb. of powder, were fired at both stations, and the velocity was deduced from the interval between the appearance of the flash and the arrival of the sound.

On this memorable occasion an observation was made which, as far as I know, has remained a scientific enigma to the present hour. It was noticed that while every report of the cannon fired at Montlhéry was heard with the greatest distinctness at Villejuif, by far the greater number of the reports from Villejuif failed to reach Montlhéry. Had wind existed, and had it blown from Montlhéry to Villejuif, it would have been recognized as the cause of the observed difference; but the air at the time was calm, the slight motion of translation actually existing being from Villejuif towards Montlhéry, or against the direction in which the sound was best heard.

So marked was the difference in transmissive power between the two directions, that on the 22nd of June, while every shot fired at Montlhéry was heard "à merveille" at Villejuif, but one shot out of twelve fired at Villejuif was heard, and that feebly, at the other station.

With the caution which characterized him on other occasions, and which has been referred to admiringly by Faraday,* Arago made no attempt to explain this anomaly. His words are: "Quant aux différences si remarquables d'intensité que le bruit du canon a toujours présentées suivant qu'il se propageaient du nord au sud entre Villejuif et Montlhéry, ou du sud au nord entre cette seconde station et la première; nous ne chercherons pas aujourd'hui à l'expliquer, parce-

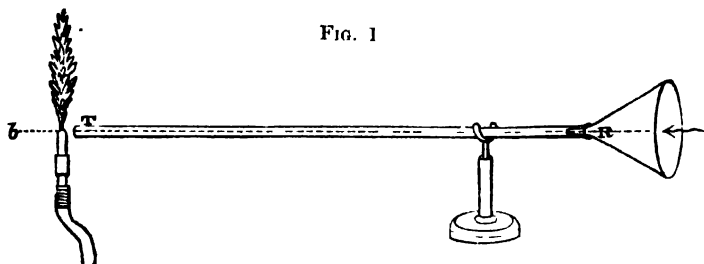
que nous ne pourrions offrir au lecteur que des conjectures denuées de preuves."*

I have tried, after much perplexity of thought, to bring this subject within the range of experiment, and have now to submit a possible solution of the enigma. The first step was to ascertain whether the sensitive flame referred to in my recent paper in the 'Philosophical Transactions' could be safely employed in experiments on the mutual reversibility of a source of sound and an object on which the sound impinges. Now the sensitive flame usually employed by me measures from 18 to 24 inches in height, while the reed employed as a source of sound is less than a square quarter of an inch in area. If, therefore, the whole flame, or the pipe which fed it, were sensitive to sonorous vibrations, strict experiments on reversibility with the reed and flame might be difficult, if not impossible. Hence my desire to learn whether the seat of sensitiveness was so localized in the flame as to render the contemplated interchange of flame and reed permissible.

The flame being placed behind a cardboard screen, the shank of a funnel passed through a hole in the cardboard was directed upon the middle of the flame. The sound-waves issuing from the vibrating reed placed within the funnel produced no sensible effect upon the flame. Shifting the funnel so as to direct its shank upon the root of the flame, the action was violent.

To augment the precision of the experiment, the funnel was connected with a glass tube three feet long and half an inch in diameter, the object being to weaken by distance the effect of the waves diffracted round the edge of the funnel, and to permit those only which passed through the glass tube to act upon the flame.

Presenting the end of the tube to the orifice of the burner (b, Fig. 1), or the orifice to the end of the tube, the flame was violently



agitated by the sounding-reed, R. On shifting the tube, or the burner, so as to concentrate the sound on a portion of the flame about half an inch above the orifice, the action was *nil*. Concentrating the sound

* 'Connaissance des Temps,' 1825, p. 370.

upon the burner itself about half an inch below its orifice, there was no action.

These experiments demonstrate the localization of "the seat of sensitiveness," and they prove the flame to be an appropriate instrument for the contemplated experiments on reversibility.

The experiments proceeded thus: The sensitive flame being placed close behind a screen of cardboard 18 inches high by 12 inches wide, a vibrating reed, standing at the same height as the root of the flame, was placed at a distance of six feet on the other side of the screen. The sound of the reed, in this position, produced a strong agitation of the flame.

The whole upper half of the flame was here visible from the reed; hence the necessity of the foregoing experiments to prove the action of the sound on the upper portion of the flame to be *nil*, and that the waves had really to bend round the edge of the screen so as to reach the seat of sensitiveness in the neighbourhood of the orifice of the burner.

The positions of the flame and reed were reversed, the latter being now close behind the screen, and the former at a distance of six feet from it. The sonorous vibrations were without sensible action upon the flame.

The experiment was repeated and varied in many ways. Screens of various sizes were employed; and instead of reversing the positions of the flame and reed, the screen was moved so as to bring, in some experiments the flame, and in other experiments the reed, close behind it. Care was also taken that no reflected sound from the walls or ceiling of the laboratory, or from the body of the experimenter, should have anything to do with the effect. In all cases it was shown that the sound was effective when the reed was at a distance from the screen and the flame close behind it; while the action was insensible when these positions were reversed.

Thus, let *se*, Fig. 2, be a vertical section of the screen. When the reed was at A and the flame at B there was no action; when the reed

FIG. 2.



was at B and the flame at A the action was decided. It may be added that the vibrations communicated to the screen itself, and from it to the air beyond it, were without effect; for when the reed, which at B is effectual, was shifted to C, where its action on the screen was greatly augmented, it ceased to have any action on the flame at A.

We are now, I think, prepared to consider the failure of rever-

sibility in the larger experiments of 1822. Happily an incidental observation of great significance comes here to our aid. It was observed and recorded at the time, that while the reports of the guns at Villejuif were without echoes, a roll of echoes, lasting from 20 to 25 seconds, accompanied every shot at Montlhéry, being heard by the observers there. Arago, the writer of the report, referred these echoes to reflection from the clouds, an explanation which I think we are entitled to regard as problematical. The report says that "*tous les coups tirés à Montlhéry y étaient accompagnés d'un roulement semblable à celui du tonnerre.*" I have italicized a very significant word—a word which fairly applies to our experiments on gun-sounds at the South Foreland, where there was no sensible solution of continuity between explosion and echo, but which could hardly apply to echoes coming from the clouds. For supposing the cloud to have been only a mile distant, the sound and its echo would have been separated by an interval of nearly ten seconds. But there is no mention of any interval; and had such existed, surely the word "followed," instead of "accompanied," would have been the one employed. The echoes, moreover, appear to have been *continuous*, while the clouds observed seem to have been *separate*. "*Ces phénomènes,*" says Arago, "*n'ont jamais eu lieu qu'au moment de l'apparition de quelques nuages.*" But from separate clouds a continuous roll of echoes could hardly come. When to this is added the experimental fact that clouds far denser than any ever formed in the atmosphere are demonstrably incapable of sensibly reflecting sound, while cloudless air, which Arago pronounced echoless, has been proved capable of powerfully reflecting it, I think we have strong reason to question the hypothesis of the French philosopher.

And considering the hundreds of shots fired at the South Foreland, with the attention specially directed to the aerial echoes, when no single case occurred in which echoes of measurable duration did not accompany the report of the gun, I think Arago's statement that at Villejuif no echoes were heard, when the sky was clear, must simply mean that they vanished with great rapidity. Unless the attention were specially directed to the point, a slight prolongation of the cannon-sound might well escape observation; and it would be all the more likely to do so if the echoes were so loud and prompt as to form apparently part and parcel of the direct sound.

I should be very loth to transgress here the limits of fair criticism, or to throw doubt, without good reason, on the recorded observations of illustrious men. Still, taking into account what has been just stated, and remembering that the minds of Arago and his colleagues were occupied by a totally different problem—that the echoes were an incident rather than an object of observation—I think we may justly consider the sound which he called "*instantaneous*" to have been one whose aerial echoes did not differentiate themselves from the direct sound by any noticeable fall of intensity, and which died rapidly into silence.

Turning now to the observations at Monthéry, we are struck by the extraordinary duration of the echoes heard at that station. At the South Foreland the charge habitually fired was equal to the largest of those employed by the French philosophers; but on no occasion did the gun-sounds produce echoes approaching to 20 or 25 seconds' duration. The time rarely reached half this amount. Even the syren-echoes, which were more remarkable and more long-continued than those of the gun, never reached the duration of the Monthéry echoes. The nearest approach to it was on the 17th of October, 1873, when the syren-echoes required 15 seconds to subside into silence.

On this same day, moreover (and this is a point of marked significance), the transmitted sound reached its maximum range, the gun-sounds being heard at the Quenocs buoy, $16\frac{1}{2}$ nautical miles distant from the South Foreland. I have stated in another place that the duration of the air-echoes indicates "the atmospheric depths" from which they come.* An optical analogy may help us here. Let light fall upon chalk, the light is wholly scattered by the superficial particles; let the chalk be powdered and mixed with water, light reaches the observer from a far greater depth of the turbid liquid. The solid chalk typifies the action of exceedingly dense acoustic clouds; the chalk and water that of clouds of moderate density. In the one case we have echoes of short, in the other echoes of long duration. These considerations prepare us for the inference that Monthéry, on the occasion referred to, must have been surrounded by a highly diacoustic atmosphere; while the shortness of the echoes at Villejuif shows the atmosphere surrounding that station to have been acoustically opaque.

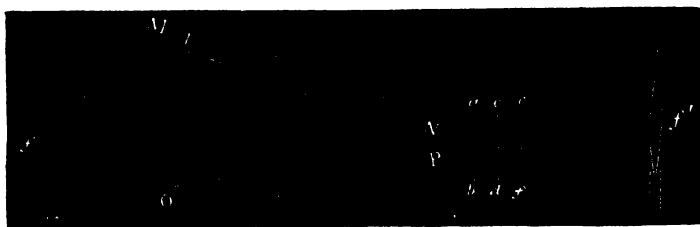
Have we any clue to the cause of the opacity? I think we have. Villejuif is close to Paris, and over it, with the observed light wind, was slowly wafted the air from the city. Thousands of chimneys to windward of Villejuif were discharging their heated currents; so that an atmosphere non-homogeneous in a high degree must have surrounded that station. At no great height in the atmosphere the equilibrium of temperature would be established. This non homogeneous air, surrounding Villejuif, is experimentally typified by our screen with the source of sound close behind it, the upper edge of the screen representing the place where equilibrium of temperature was established in the atmosphere above the station. In virtue of its proximity to the screen, the echoes from our sounding-reed would, in the case here supposed, so blend with the direct sound as to be practically indistinguishable from it, as the echoes at Villejuif followed the direct sound so hotly, and vanished so rapidly, that they escaped observation. And as our sensitive flame, at a distance, failed to be affected by the sounding body placed close behind the cardboard screen, so, I take it, did the observers at Monthéry fail to hear the sounds of the Villejuif gun.

* 'Phil. Trans.' 1874, pt. i. p. 202.

Something further may be done towards the experimental elucidation of this subject. The facility with which sounds pass through textile fabrics has been already illustrated,* a layer of cambric or calico, or even of thick flannel or baize, being found competent to intercept but a small fraction of the sound from a vibrating reed. Such a layer of calico may be taken to represent a layer of air differentiated from its neighbours by temperature or moisture; while a succession of such sheets of calico may be taken to represent successive layers of non-homogeneous air.

Two tin tubes (M N and O P, Fig. 3) with open ends were placed so as to form an acute angle with each other. At the end of one was the vibrating reed *r*; opposite the end of the other, and in the prolongation of P O, the sensitive flame *f*, a second sensitive flame (*f'*) being placed in the continuation of the axis of M N. On sounding the reed, the direct sound through M N agitated the flame *f'*. Introducing the square of calico *a b* at the proper angle, a slight decrease of the

FIG. 3.



action on *f'* was noticed, and the feeble echo from *a b* produced a barely perceptible agitation of the flame *f*. Adding another square, *c d*, the sound transmitted by *a b* impinged on *c d*; it was partially echoed, returned through *a b*, passed along P O, and still further agitated the flame *f*. Adding a third square, *e f*, the reflected sound was still further augmented, every accession to the echo being accompanied by a corresponding withdrawal of the vibrations from *f'* and a consequent stilling of that flame.

With thinner calico or cambric, it would require a greater number of layers to intercept the entire sound; hence with such cambric we should have echoes returned from a greater distance, and therefore of greater duration. Eight layers of the calico employed in these experiments, stretched on a wire frame and placed close together as a kind of pad, may be taken to represent a dense acoustic cloud. Such a pad, placed at the proper angle beyond N, cuts off the sound, which in its absence reaches *f'*, to such an extent that the flame *f'*, when not too sensitive, is thereby stilled, while *f* is far more powerfully agitated than by the reflection from a single layer. With the source

* 'Phil Trans' 1874, pt. i. p. 208.

of sound close at hand, the echoes from such a pad would be of insensible duration. Thus close at hand do I suppose the acoustic clouds surrounding Villejuif to have been, a similar shortness of echo being the consequence.*

A further step is here taken in the illustration of the analogy between light and sound. Our pad acts chiefly by internal reflection. The sound from the reed is a composite one, made up of partial sounds differing in pitch. If these sounds be ejected from the pad in their pristine proportions, the pad is acoustically *white*; if they return with their proportions altered, the pad is acoustically *coloured*.

In these experiments my assistant, Mr. Cottrell, has rendered me material assistance.

[J. T.]

* Since this was written I have sent the sound through fifteen layers of calico, and echoed it back through the same layers, in strength sufficient to agitate the flame. Thirty layers were here crossed by the sound. The sound was subsequently found able to penetrate two hundred layers of cotton net; a single layer of wetted calico being competent to stop it.

Friday, March 5, 1875.

GEORGE BUSK, Esq. F.R.S. Treasurer and Vice-President,
in the Chair.

THE LORD RAYLEIGH, M.A. F.R.S. M.R.I.

On the Dissipation of Energy.

THE second law of thermodynamics, and the theory of dissipation founded upon it, has been for some years a favourite subject with mathematical physicists, but has not hitherto received full recognition from engineers and chemists, nor from the scientific public. And yet the question under what circumstances it is possible to obtain work from heat is of the first importance. Merely to know that when work is done by means of heat, a so-called equivalent of heat disappears is a very small part of what it concerns us to recognize.

A heat engine is an apparatus capable of doing work by means of heat supplied to it at a high temperature and abstracted at a lower, and thermodynamics shows that the fraction of the heat supplied capable of conversion into work depends on the limits of temperature between which the machine operates. A non-condensing steam engine is not, properly speaking, a heat engine at all, inasmuch as it requires to be supplied with water as well as heat, but it may be treated correctly as a heat engine giving up heat at 212° Fahr. This is the lower point of temperature. The higher is that at which the water boils in the boiler, perhaps 360° Fahr. The range of temperature available in a non-condensing steam engine is therefore small at best, and the importance of working at a high pressure is very apparent. In a condensing engine the heat may be delivered up at 80° Fahr.

It is a radical defect in the steam engine that the range of temperature between the furnace and the boiler is not utilized, and it is impossible to raise the temperature in the boiler to any great extent, in consequence of the tremendous pressure that would then be developed. There seems no escape from this difficulty but in the use of some other fluid, such as a hydrocarbon oil, of much higher boiling point. The engine would then consist of two parts—an oil engine taking in heat at a high temperature, and doing work by means of the fall of heat down to the point at which a steam engine becomes available, and secondly a steam engine receiving the heat given out by the oil engine and working down to the ordinary atmospheric temperature.

Heat engines may be worked backwards, so as by means of work to raise heat from a colder to a hotter body. This is the principle of the air or ether freezing machines now coming into extensive use. In this application a small quantity of work goes a long way, as the range of temperature through which the heat has to be raised is but small.

If the work required for the freezing machine is obtained from a steam engine, the final result of the operation is that a fall of heat in the prime mover is made to produce a rise of heat in the freezing machine, and the question arises whether this operation may be effected without the intervention of mechanical work. The problem here proposed is solved in Carré's freezing apparatus, described in most of the text-books on heat. There are two communicating vessels, A and B, which are used alternately as boiler and condenser. In the first part of the operation aqueous ammonia is heated in A, until the gas is driven off and condensed under considerable pressure in B, which is kept cool with water. Here we have a fall of heat, the absorption taking place at the high temperature and the emission at the lower. In the second part of the operation A is kept cool, and the water in it soon recovers its power of absorbing the ammonia gas, which rapidly distils over. The object to be cooled is placed in contact with B, and heat passes from the colder to the hotter body. Finally the apparatus is restored to its original condition, and therefore satisfies the definition of a heat engine. M. Carré has invented a continuously working machine on this principle, which is said to be very efficient.

Other freezing arrangements depending on solution or chemical action may be brought under the same principle, if the cycle of operations be made complete.

When heat passes from a hotter to a colder body without producing work, or some equivalent effect such as raising other heat from a colder to a hotter body, energy is said to be dissipated, and an opportunity of doing work has been lost never to return. If on the other hand the fall of heat is fully utilized, there is no dissipation, as the original condition of things might be restored at pleasure; but in practice the full amount of work can never be obtained, in consequence of friction and the other imperfections of our machines.

The prevention of unnecessary dissipation is the guide to economy of fuel in industrial operations. Of this a good example is afforded by the regenerating furnaces of Mr. Siemens, in which the burnt gases are passed through a passage stacked with fire-bricks, and are not allowed to escape until their temperature is reduced to a very moderate point. After a time the products of combustion are passed into another passage, and the unburnt gaseous fuel and air are introduced through that which has previously been heated. The efficiency of the arrangement depends in great degree on the fact that the cold fuel is brought first into contact with the colder parts of the flue, and does not take heat from the hotter parts until it has itself become hot.

In this way the fall of heat is never great, and there is comparatively little dissipation.

The principal difficulty in economy of fuel arises from the fact that the whole fall of heat from the temperature of the furnace is seldom available for one purpose. Thus in the iron smelting furnaces heat below the temperature of melting iron is absolutely useless. But when the spent gases are used for raising steam, the same heat is used over again at another part of its fall. There is no reason why this process should not be carried further. All the heat discharged from non-condensing steam engines, which is more than nine-tenths of the whole, might be used for warming or drying, or other operations in which only low temperature heat is necessary.

The chemical bearings of the theory of dissipation are very important, but have not hitherto received much attention. A chemical transformation is impossible, if its occurrence would involve the opposite of dissipation (for which there is no convenient word); but it is not true, on the other hand, that a transformation which would involve dissipation must necessarily take place. Otherwise the existence of explosives like gunpowder would be impossible. It is often stated that the development of heat is the criterion of the possibility of a proposed transformation, though exceptions to this rule are extremely well-known. It is sufficient to mention the solution of a salt in water. This operation involves dissipation, or it would not occur, and it is not difficult to see how work might have been obtained in the process. The water may be placed under a piston in a cylinder maintained at a rigorously constant temperature, and the piston slowly raised until all the water is evaporated, and its tension reduced to the point at which the salt would begin to absorb it at the temperature in question. After the salt and vapour are in contact the piston is made to descend until the solution is effected. In this process work is gained, since the pressure under the piston during the expansion is greater than at the corresponding stage of the contraction. If the salt is dissolved in the ordinary way energy is dissipated, an opportunity of doing work at the expense of low temperature heat has been missed and will not return.

The difficulty in applying thermodynamical principles to chemistry arises from the fact that chemical transformations cannot generally be supposed to take place in a reversible manner, even although unlimited time be allowed. Some progress has, however, recently been made, and the experiments of Debray on the influence of pressure on the evolution of carbonic anhydride from chalk throw considerable light on the matter. By properly accommodating the pressure and temperature, the constituents of chalk may be separated or recombined without dissipation, or rather dissipation may theoretically be reduced without limit by making the operation slowly enough.

The possibility of chemical action must often depend on the density of the reacting substances. A mixture of oxygen and hydrogen in the

proper proportions may be exploded by an electric spark at the atmospheric pressure, and energy will be dissipated. In this operation the spark itself need not be considered, as a given spark is capable of exploding any quantity of gas. Suppose, now, that previously to explosion the gas is expanded at constant temperature, and then after explosion brought back to the former volume. Since in the combination there is a condensation to two-thirds, the pressure required to compress the aqueous vapour is less than that exercised at the same volume by the uncombined gases, and accordingly work is gained on the whole. Hence the explosion in the expanded state involves less dissipation than in the condensed state, and the amount of the difference may be increased without limit by carrying the expansion far enough. It follows that beyond a certain point of rarity the explosion cannot be made, as it could not then involve any dissipation. But although the tendency to combine diminishes as the gas becomes rarer, the heat developed during the combination remains approximately constant.

It must be remembered that the heat of combination is generally developed at a high temperature, and that therefore work may be done during the cooling of the products of combustion. If, therefore, it is a necessity of the case that the act of combustion should take place at a high temperature, the possibility of explosion will cease at an earlier point of rarefaction than would otherwise have been the case.

It may probably be found that many mixtures which show no tendency to explode under ordinary conditions will become explosive when sufficiently condensed.

[R.]

Friday, April 30, 1875.

WARREN DE LA RUE, Esq. D.C.L. F.R.S. Vice-President,
in the Chair.

WALTER NOEL HARTLEY, F.C.S.

DEMONSTRATOR OF CHEMISTRY, KING'S COLLEGE, LONDON,

On the Action of Heat on Coloured Liquids.

ALL substances whatever may be divided into two classes, the coloured and the colourless. By simple inspection it is impossible to distinguish one colourless liquid from another, but the case is very different with coloured substances. In dealing with compound substances derived from the metals, we find generally that a certain colour is characteristic of a certain metal. Thus a blue is the tint which prevails in most compounds containing copper, while green is characteristic of nickel, and pink or red of cobalt. If we examine the colour of a metallic solution by transmitting light through it, and analyzing this light with a prism, as Dr. Gladstone did in the year 1857,* we then get a spectrum which serves in some degree to identify the metal present in the solution. Taking, for example, three liquids containing the same metal—a green, a purple, and a red solution—the green chloride, the purple sulphate, and the red oxalate of chromium, we have such a diversity of behaviour with chemical reagents, and such a variety of tints, that it is not an easy matter to recognize the presence of the same base unless the light transmitted by those solutions is analyzed by the prism, and if this be done in a wedge-shaped cell, we have the advantage of seeing through many different thicknesses of liquid at one glance. We then get a spectrum in each case with chromium compounds, which has a great similarity, its chief characteristic being that the red, green, and blue rays are transmitted, while all the yellow are cut out. It has long been known that certain metallic solutions darken on exposure to heat, and in this way prisoners sometimes effect a secret correspondence outside the prison walls. The method consists in writing with an invisible solution between the lines of their letters, which is afterwards developed by those who are in the secret. Such solutions have been called sympathetic inks, and one in particular, called Hellot's sympathetic ink, is

* Proceedings of the Royal Institution

the chloride of cobalt, which being of a pale pink colour, in the state of a dilute solution, on drying and heating turns a very dark blue. Writing executed with this ink is all but invisible until a hot iron be passed over it, when it appears beautifully distinct, and on cooling disappears again. The Fenian criminal, Barrett, when confined in the House of Detention, was found to have in his possession a small tube containing chloride of gold: in the woollen stockings sent to him was noticed some white powder, which could be shaken out. This was evidently for the purpose of secret correspondence. The powder was found to be sulphate of iron; writing with a dilute solution of chloride of gold would be invisible until washed over with sulphate of iron, which solution developes the characters. The blue colour of cobalt chloride (Hellot's ink) is more easily produced if the salt be mixed with calcium chloride; such a mixture is that used for the little instrument called the chameleon barometer. This, which is in reality a hygrometer, or an indicator of the amount of moisture in the air, consists simply of a piece of paper soaked in the two solutions, protected by a glass and frame. The way in which it is differently affected by dry and moist air may be easily seen. Placing two of these under different bell-jars, one containing a little vessel of oil of vitriol, which dries the air, the other a little water, which of course keeps it moist, the paper in the former will be blue, and that in the latter red; then, if their places be changed their colours change. That a solution of cobalt chloride could be turned blue by the addition of hydrochloric acid, of sulphuric acid, of alcohol, or of chloride of calcium, has for some time been known; it has also been noticed that an acid solution of chloride of cobalt, red at an ordinary temperature, becomes blue if heated, such being also the case with a dilute solution containing alcohol; furthermore, that a dilute solution, if heated under pressure in sealed tubes to a higher temperature than that of boiling water, becomes blue.

In 1871 I found that a strong perfectly neutral aqueous solution of the purest cobalt chloride, which had been prepared from Claudet's salt, changed colour with the greatest possible ease upon heating. A small tube-full held in the hand changed from deep crimson to a decided purple tint in a few minutes; a little of the solution smeared over the fingers soon became blue; and a quantity of the liquid heated in an open dish became blue at 70° C. It was noticed that a very small tube of flattened glass, containing a solution of cobalt chloride, which was perfectly transparent when cold, upon heating to 70° C. became quite opaque. It was evident that the change from red to blue noticed was not simply a difference in refrangibility of the transmitted light, but an increase in the quantity of light absorbed by the solution. Hence it appeared to be a matter of great interest to examine the change of colour by means of the spectroscope, and even to go beyond this, and examine the action of heat on all coloured liquids by the same means, but especially was it expected that the bromide and iodide of cobalt would yield intensified

effects of the same kind. Observations have been made on about sixty different solutions, most of which were prepared from metallic salts. Many of these compounds had been but imperfectly examined, while others were quite new. The solutions were generally made by allowing cold water to stand for some days with the crystallized salt, giving it frequent agitation.

The examinations were made in wedge cells cut out of blocks of glass, and polished; one side of the cell was made by fixing on a piece of plate-glass by means of a screw clamp. Two sizes of these hollow wedges were used to facilitate the examination of liquids of different intensities of colour. They were each of the same height, namely, three-quarters of an inch, the larger cells being at their thickest part three-quarters of an inch, diminishing to nothing; the smaller being not more than three-sixteenths of an inch thick. The refraction caused by the thick wedge of liquid was corrected by the wedge of glass which formed one side of the cell. A little copper hot-air cupboard, with two opposite sides of easily removable plates of glass, was used for heating the wedges filled with liquid. These wedges were covered with plates of glass, as far as possible to prevent evaporation. Sunlight was used when possible, and in many cases when this was impossible an argand gas burner was used, of such a construction that oxygen gas could be blown into the flame to increase the brilliancy and whiteness of the light.

The spectra of metallic solutions were noticed as being principally of three kinds: those caused by the uninterrupted transmission of certain rays, such as the blue by salts of copper and the green by nickel; those consisting of continuous spectra interrupted by sharp black bands, such as didymium and uranium salts yield; and those resulting from two groups of rays of different refrangibilities, as the green and red seen in chromium salts, and the blue and red in cobalt compounds. Such spectra are those of dichroic solutions. The difference between monochroic and dichroic solutions is easily shown in the following manner, thus: when the spectrum of the electric lamp is thrown on to the screen, and a cell containing sulphate of copper or nickel is interposed, a simple green band of light appears; if, instead of a spectroscopic slit, a round disk is used, only one image of this is seen; and if the image of the carbon points of the electric lamp be thrown on to the screen, when a prism is interposed containing nickel solution, one image, and that a green one, is formed. Taking a dichroic liquid such as chrome alum, we get a spectrum consisting of red and green rays, separated by a band of darkness; a disk of light becomes resolved into two, one of a rich red and the other of a green tint, both colours of great beauty; where the two disks overlap the original colour of the liquid is formed.

If we project the image of the carbon points through a hollow prism of the liquid, two images are formed, one red, the other green. Precisely the same thing occurs with cobalt chloride, but the two colours are purple and orange.

The amount of absorption of light taking place in different thicknesses of a solution is easily observed when wedge cells are used, and it is thus easy to ascertain what change will take place on diluting the liquid, provided water is without chemical action. Liquids presenting a wedge-shaped spectrum alter in colour on dilution, in the ratio indicated by the relation of the angle of the wedge-shaped spectrum to that of the wedge cell. These solutions, having spectra bounded by perpendicular straight lines, are only slightly affected by dilution. Some crystallized chromate of potash was dissolved in as little water as possible, forming a beautiful canary yellow colour. This, when diluted to 12,000 times the original weight of the salt, was not greatly altered, the change being not in depth of tint but in brilliancy. Permanganate of potash shows five black lines in the green portion of the spectrum when much diluted with water, and three of these are perfectly well seen when looking through half an inch of liquid which contains only one part of the salt in 118,000 parts of water. The loss of colour caused by the dilution of ammonio-chloride of palladium is indicated by its wedge-shaped spectrum, and was illustrated by dissolving one grain weight of the salt in water and diluting the dark brown liquid till the colour disappears; a pint and a half of water was sufficient for the purpose. On repeating the experiment with permanganate of potash the liquid remained of a beautiful pink colour, even after five gallons of water had been added.

It is a remarkable fact, that although the first step in practical chemistry is the solution of a substance in water, it has hitherto not been ascertained what really takes place when this operation is performed, consequently we are in ignorance of the chemical constitution of the resulting liquid. The chief reason for undertaking this investigation was the hope that this question, to which very doubtful and unsatisfactory answers could alone be given, might be finally decided, and the work recorded has been well bestowed on the subject.

Most metallic salts form combinations with water; the ordinary carbonate of soda (washing soda) is the carbonate of the metal united with ten molecules of water, which may be separated in the form of steam by heating to 100° C. It therefore contains not far from two-thirds of its weight of water, and many other salts combine with water in the same way. Carbonate of soda, however, is colourless; but many *coloured* substances combine with different proportions of water to form compounds varying in colour; thus we see in the accompanying tabular statement the variation between the colour of the anhydrous salts and their different combinations with water are very striking. Many compounds do not lose all their combined water at 100° C., and these salts are amongst the number.

It is a remarkable fact the substances named in the following table are those which change colour most notably on heating their solutions, hence a number of conclusions have been arrived at as to the internal or molecular structure of these solutions. The spectroscope itself would be quite unavailable in giving us the desired information; but chemical

SUBSTANCES VARYING IN COLOUR,

Anhydrous		Compounds produced at 100° C. from ordinary Crystals.	
CuCl ₂	Yellow	CuCl ₂ · H ₂ O
CuBr ₂	Black and lustrous	CuBr ₂ · H ₂ O	Dark brown
CoCl ₂	Lavender; blue when hot ..	CoCl ₂ · 2H ₂ O	Purple; blue when hot
CoBr ₂	Vivid green	CoBr ₂ · 2H ₂ O	Purple; blue when hot
CoI ₂	Lustrous intense black ..	CoI ₂ · 2H ₂ O	Moss-green
NiBr ₂	Yellow	(NiBr ₂ · H ₂ O?)	Dark red
NiI ₂	Lustrous intense black ..	(NiI ₂ · 2H ₂ O?)	Dark brown

research, aided by the observation of optical properties, yields what neither alone could do.

A distinct statement regarding this action of heat here follows :

The effect of Heat on Absorption-spectra.

When saturated solutions of coloured salts are heated to 100° C., 1st, there are few cases in which no change is noticed. 2ndly, generally the amount of light transmitted is diminished to a small extent by some of the more refrangible, the less refrangible, or both kinds of rays being obstructed. 3rdly, there is frequently a complete difference in the nature of the transmitted light. Anhydrous salts not decomposed, hydrated compounds not dehydrated at 100° C., and salts which do not change colour on dehydration, give little or no alteration in their spectra when heated.

Solutions of hydrated salts, and most notably those of haloid compounds, do change ; and the alteration is, if not identical with, similar to that produced by dehydration and the action of dehydrating liquids, such as alcohol, acids, and glycerine, on the salts in crystals or solution.

A particularly interesting instance of the action of heat on an aqueous solution is that of cobalt chloride, which gives a different series of dark bands in the red part of the spectrum at different temperatures, ranging between 23° C. and 73° C. Band after band of shadow intercepts the red rays as the temperature rises, till finally nothing but the blue are transmitted. Drawings of six different spectra of this remarkable nature have been made. The changes are most marked between 33° and 53°, when the temperature may be told almost to a degree by noting the appearance of the spectrum. Though to the unaided eye cobalt bromide appears to undergo the same change, yet, as seen with the spectroscope, it is not of so curious a character, the bands being not so numerous.

With cobalt iodide a band of red and green rays is transmitted at

WITH THEIR STATE OF HYDRATION.

Ordinary Crystals.			Colour of Solution.		
			Strong.	Dilute.	
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Blue		Grass green	Blue.	
$\text{CuBr}_2 \cdot 5\text{H}_2\text{O}$	Golden green		Red brown	Blue.	
$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$	Cherry red		Deep red	Pink.	
$\text{CoBr}_2 \cdot 6\text{H}_2\text{O}$	Deep crimson		Deep crimson	Pink.	
$\text{CoI}_2 \cdot 6\text{H}_2\text{O}$	Dusky red-brown		Dark brown	Pink.	
$\text{NiBr}_2 \cdot 3\text{H}_2\text{O}$	Green		Madder brown	Apple green.	
$\text{NiI}_2 \cdot 6\text{H}_2\text{O}$	Bluish green		Yellowish brown	Apple green.	

low temperatures; the band of light moves towards the opposite end of the spectrum, with rise of temperature, until it is transferred to such a position that it consists of green rays only. In this instance the change to the eye is more striking when seen without the spectroscope, because the mixtures of red, yellow, and green rays, which are formed during the transition, give rise to very beautiful shades of brown and olive green. Thus a saturated solution at 16°C . was of a brown colour, at -10°C . it became of a fiery red and crystals separated, at $+10^\circ$ reddish brown, at 20° the same, at 35° vandyke brown, at 45° a cold brown tint with a tinge of yellowish green, at 55° a decidedly yellowish green in thin layers and yellow brown in thick, at 65° greenish brown, thin layers green, and at 75° olive green. This was shown by heating a little of the liquid in a globular flask while it was rapidly rotated by the hand, the liquid thus being spread in a thin layer over a large surface. An examination of this cobalt salt has shown that there are two distinct crystalline hydrates—the one, formed at high temperatures, has the formula $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$, and is of a dark green colour; the other, which contains a much larger proportion of crystalline water, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, is produced at a low temperature, and its colour is generally brown, in cold weather inclining to red.

The formation of the dihydrate and the anhydrous compound was beautifully shown in the following manner: A glass plate, upon which was smeared a thin but even layer of the cobalt iodide, was held in the rays of the electric light projected on to a screen. At first nothing was to be seen, but on warming the plate a spot of greenish yellow light appeared, and this spreading in every direction showed itself to be a mass of green crystals; the application of a little more heat soon converted these into the black anhydrous compound.

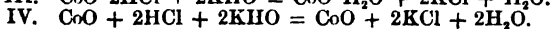
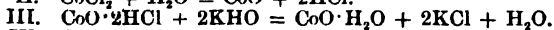
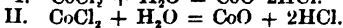
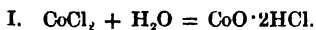
In the case of didymium nitrate a new line was seen to come into existence. The instances of the third kind were frequently so altered by heat, that the less refrangible group of rays was extinguished partially, if not entirely. Cobalt and chromium compounds furnish examples of this.

The formation of different hydrates of the same salt, each of which has its characteristic colour, is very strikingly shown with bromide and iodide of cobalt; thus a sketch of sea and sky is made with the former, the liquid is pink, and not strong in colour, so that very little is seen until the paper be warmed, when the most beautiful azure tints appear. If carefully managed, the green anhydrous compound may be produced, and so give a greenish tinge to the sea. The red hexahydrate of cobalt bromide is first converted into the blue dihydrate, and then into the green anhydrous compound. But an infinitely more astonishing change is that produced by warming a sketch of foliage and water made with the iodide and bromide of cobalt. It has the appearance of a warm-tinted sepia drawing, which gives the foliage quite an autumnal appearance. On warming, the blue of the sky and water, together with exquisite green tints in the foliage, appear. By varying the quantity of the cobalt iodide put on with the brush, colours varying between the most delicate green of spring-time, the full richness of summer, and all kinds of greenish brown autumnal tints, even black, may be produced. The atmospheric moisture re-forms the original hexahydrated salts, and the colours disappear when the paper gets cold again. Two sketches of this kind were exhibited which resumed their original brown colour in the course of half an hour.

It has been suggested, even quite lately, that when a salt such as a chloride is dissolved in water, it is resolved into a hydrochlorate of a metallic oxide, and that hydrated chlorides are always compounds of this kind. Hence, when cobalt chloride is dissolved in water, change from pink to blue might be owing to the alteration in the dissolved compound, from a hydrochlorate of cobalt oxide to a cobalt chloride.

The first step to be taken is the refutation of this. When a solution of cobalt chloride, bromide, or iodide is dissolved in water, and cold alkali, such as potash or soda added, the precipitate formed is not, as one would expect, a hydrate or an oxide, but an oxy-chloride, oxy-bromide, or oxy-iodide, showing that in solution the halogen is still combined with the metal, and is only partially removed by the more powerful base. Similar basic compounds are formed by precipitating other cobalt solutions, such as nitrate.

Equations I. and II. illustrate the supposed and possible decomposing action of water on cobalt chloride, while III. and IV. show the reactions with alkali which would consequently take place; but as these latter do not represent the truth, it necessarily follows that the former are incorrect.



I. Hence we may conclude that when a salt is dissolved in water it is not decomposed into a mixture of an oxide and an acid, nor does a compound of the oxide with the acid result.

II. When a salt is dissolved in water it does not necessarily attain its maximum state of hydration.

This was long ago suspected by Dr. Gladstone, who, experimenting with cupric chloride, found that a saturated solution of a deep green colour became blue on the addition of water, and this blue became green again upon heating. Furthermore, the blue liquid could be turned to green by the addition of strong hydrochloric acid. These facts of course have been corroborated by spectroscopic observations, and I have succeeded in obtaining others in support of this. Thus the following saturated solutions change colour when diluted with from four to seven times their bulk of water :

Saturated Solution.	Colour.	Dilute Solution—Colour
Cupric chloride ..	Grass green	Blue.
" bromide ..	Deep red-brown ..	Yellowish green to azure blue.
Nickel ..	Dark madder brown	" apple green.
" iodide ..	Yellowish brown ..	" "

As illustrations two cylinders were taken, one containing cupric chloride, the other cupric bromide; the former grass green, and the latter deep brown. The colours were shown by swilling the liquid round the sides of the vessels; on dilution with about a quart of water clear azure blue liquids were produced.

A still more striking example is that of the cobalt iodide solution, which is formed by allowing the dihydrate, or the anhydrous salt to deliquesce; it is of a deep green, and on dilution to a very small extent becomes red.

Regnault and also Person have shown that on diluting a saturated solution of a salt, as a rule there is an absorption of heat. The latter calls this the latent heat of dilution. The former noticed one or two cases in which heat was evolved on dilution. There is every likelihood that this phenomenon is due to the formation of a liquid hydrate. It is impossible of belief that accompanying such a circumstance there should be no measurable development of heat; and these experiments have proved that in all cases when the change of colour consequent on dilution is great, the heat disengaged is very considerable. On diluting a solution of cobalt iodide till the red colour appears, the thermal effect not only registers several degrees on an ordinary thermometer, but it may be perceived by the hand.

The author has not yet completed any exact thermal measurements bearing on this matter, though some experiments have been made in this direction.

III. When a hydrated salt is dissolved in water to form a saturated solution at the ordinary temperature its crystalline molecule remains chemically intact, except in certain exceptional cases, when it appears to lose water.

The evidence bearing on this consists of the fact that most solutions of hydrated salt, if saturated, are of the same colour as the solid compound; though in the state of dilute solutions on the one hand, or of partial dehydration on the other, the colour may differ widely from this. In support of this we have the case of cobalt chloride and cobalt iodide, more especially the formation and behaviour of the green solution of the dihydrate of the latter salt. The molecule of the salt is neither hydrated nor dehydrated on solution, otherwise such salts as those named would change colour.

An exceptional phenomenon is marked when cupric chloride, cupric bromide, nickel bromide, and nickel iodide are dissolved in water to saturation. Cupric chloride is a blue salt not deliquescent or liable to absorb water from the air, but rather efflorescent, i. e. apt to part with its water of crystallization; hence, when the blue crystals are dissolved in water they form a deep green liquid, which on dilution becomes azure blue, this azure blue solution by heating again becomes green. The remaining salts are of a yellowish green tint, but on dissolving in as little cold water as possible they give intensely coloured brown liquids. Cupric bromide crystals effloresce, losing 10 per cent. of water, and becoming very dark brown, nearly as possible black in colour even in ordinary air, but in presence of moisture they are deliquescent.

Solution facilitates chemical change. Hence, when green cupric bromide crystals are dissolved in water the chemical attraction which binds the one molecule of metallic bromide to the five molecules of water of crystallization is so weakened that the cohesive attraction of the mass of the solvent water overcomes the chemical attraction of the crystalline water, and the resulting liquid is brown. When more water, however, is added a reversion of this action takes place, and the brown solution becomes green or blue.

IV. When a salt forms two distinct crystalline hydrates, A and B, at temperatures below 100° C., a saturated solution of A will, on heating to 100° , become a solution of B; at intermediate temperatures, a mixture of these two compounds.

This is inferred from the similarity in change of colour of a saline solution to the change of colour in the solid when heated. Bromide and chloride of copper, and, above all, iodide of cobalt, exhibit such changes.

The behaviour of this latter salt, which has been already mentioned, cannot possibly be explained except by the assumption that the hexahydrate, $\text{CoI}_2 \cdot 6\text{H}_2\text{O}$, exists in the brown solution, and the dihydrate, $\text{CoI}_2 \cdot 2\text{H}_2\text{O}$, in the green liquid produced from this by heat. The action of heat on cobalt chloride is not so well defined; that it is caused by dehydration we are certain, but whether the compound in solution is the dihydrate or the anhydrous chloride is a matter undetermined. It is not at all unlikely that the blue produced by alcohol is due to the formation of an alcoholate, for the spectrum, though very similar, is not quite identical with that of the hot aqueous

solution. An experiment made on the hexahydrate was incidentally confirmatory of the action of water on the cupric chloride and bromide. When this salt was dissolved nearly to saturation in absolute alcohol the liquid had the usual magnificent blue colour; it was put aside under a bell-glass for crystals to separate, these appeared at the bottom of the deep blue liquid to be also of the same colour. When removed, however, and pressed between folds of paper, they had precisely the same composition and red colour as the original salt. Hence, though water could not on solution remove the water of crystallization from the salt, yet alcohol could do this, but on crystallization the original crystalline hydrate was formed, as is the case with cupric chloride and bromide.

V. The effect of heat on what are called the purple chromium solutions is not traced to dehydration, but to a distinct chemical reaction which yields a distinct class of compounds.

The violet or purple compounds of chromium have the general formula $\text{Cr}'''\text{R}_3 \cdot x\text{H}_2\text{O}$, or $\text{Cr}_2'''\text{R}''_3 \cdot x\text{H}_2\text{O}$; when solutions of these in water are heated to 100°C . there is formed a class of substances which may be written thus, $\text{Cr}_2'''\text{OR}_4 \cdot x\text{H}_2\text{O}$, and $\text{Cr}_2'''\text{OR}''_2 \cdot x\text{H}_2\text{O}$, or the first compounds may be said to contain the metal Cr''' as the base of the compound, while the second contain the radical $\text{Cr}_2'''\text{O}$. This radical I would propose to call chromyl, just as UO is called uranyl. And it may then be stated, that while the purple compounds are salts of chromium, the green are salts of chromyl.

This conclusion is derived more from the chemical behaviour of these solutions than from their optical properties. Thus green solutions having the same spectrum may be produced from the sulphate or nitrate—(1) by boiling a solution of the purple salt; (2) by dissolving an excess of chromic hydrate in the purple solution; (3) by neutralizing with an alkali one-third of the acid in a solution of the blue salts. 50" of a boiled solution containing half a gramme of the sulphate or nitrate of chromium will not give a precipitate if boiled with two or three litres of water; but when one-third of the acid present has been previously neutralized, or when an excess of chromic hydrate is dissolved in the blue solution, a basic salt is thrown down on boiling with much water. This is exactly the behaviour characteristic of a salt described by Schröter, to which he assigns the formula $\text{Cr}_2\text{O}_3 \cdot 2\text{SO}_3$, or which may be written $\text{Cr}_2\text{O} \cdot 2\text{SO}_3$. Læwel describes a similar chloride, which is formed at 100°C .; this he writes thus, $\text{Cr}_2\text{O}_3 \cdot 4\text{HCl}$, and the formula may be modified in the following manner, $\text{Cr}_2\text{O} \cdot \text{Cl}_4 \cdot 2\text{H}_2\text{O}$. The modification has the following recommendation—that it explains the decomposition of the substance when heated to a high temperature, which Læwel's formula does not. At or about 300°C . the compound is resolved into a mixture of the anhydrous violet compound of chromium and chlorine, CrCl_3 , or Cr_2Cl_6 , and the anhydrous green oxide, Cr_2O_3 ; if the original salt were a combination simply of hydrochloric acid with chromic oxide, heating would drive off the volatile acid and leave the oxide only, but

the actual change indicates that the chromium and chlorine are in direct combination.

Having thus brought forward a new, if limited, application of spectrum analysis to chemical research, it is only necessary to add that the field of inquiry thus commenced is by no means exhausted. It has long been the writer's intention to add new facts to the study of organic chemistry by examining the invisible photographic spectra of colourless carbon compounds, but one pair of hands in the leisure hours of a not too long vacation cannot keep pace with one's ideas.

[W. N. H.]

Friday, May 7, 1875.

GEORGE BUSK, Esq. F.R.S. Treasurer and Vice-President,
in the Chair.

PROFESSOR A. CORNU,

PROFESSOR AT THE POLYTECHNIC SCHOOL, AND COUNCILLOR OF THE PARIS OBSERVATORY,

On New Determinations of the Velocity of Light.

THE old philosophers and astronomers, until Galileo, thought that the propagation of light was instantaneous.

Astronomical Determination of the Velocity of Light.—Rømer, a Danish astronomer, called to the Paris Observatory by the illustrious Picard, after having computed from some old observations the eclipse times of Jupit. r's satellites, found great discrepancies between the calculated and observed times: the eclipses appear too soon when Jupiter approaches the earth and too late when it goes away. Rømer ascribed these differences to the time necessary for the propagation of light, and concluded from his observations that light requires about eight minutes to come from the sun to the earth.

Bradley, one of the most illustrious English astronomers, seeking to put in evidence certain small annual motions of the stars caused by the displacement of the earth in space (annual parallax), found such a motion, but quite different from the expected one. The apparent deflection of the direction of a star—for instance, γ Draconis, near the pole of the ecliptic—instead of being at every moment directed, as expected, towards the centre of the terrestrial orbit (the sun), is directed at a right angle. The greatest elongation (called *aberration*) rises to $40.7''$ from six to six months. Bradley, after many attempts, ascribed this effect to the composition of the velocity of light with the velocity of the elliptic motion of the earth (1728).

From those observations, and from the approximate knowledge of the distance from the sun to the earth, the velocity of light was found equal to about 200,000 *English miles in a second*, in other terms, *one million times the velocity of sound*.

Direct Determinations of the Velocity of Light were for a long time considered as impossible, owing to the enormous value of this velocity. The first solution was given by M. Fizeau (1849) by the method of the *toothed wheel*.

Induced by some considerations analogous to the celebrated *accès theory* of Newton, M. Fizeau, one of the most illustrious members

of the Paris Academy, and recently elected Honorary Member of the Royal Society, succeeded in rendering perceptible and even measurable the duration of the propagation of light for a distance of a few miles.

The principle of the method is the following :

A beam of light passes through the interval between two teeth of a rotative toothed wheel (*roue dentée*) : this beam is reflected on a mirror fixed some miles distant, comes back exactly on the same line, and passes again through the same interval as before. An observer can receive this beam : he will see a luminous point, a *luminous echo*, through each hollow between two teeth : if the wheel revolves with an increasing speed the luminous impression will first become continuous. The wheel will soon revolve with sufficient rapidity to turn a small angle during the time necessary for the beam of light to go and come back again. The angular velocity can be so regulated that the solid part of a tooth is substituted for the hollow part during this time ; then, on coming back, the beam will be obstructed by the wheel. The same obstruction will take place at each tooth, and the luminous echo will disappear.

If the velocity of the wheel be doubled, the luminous point will appear again, because the reflected beams will meet with the following hollow and pass through. With a triple velocity a new extinction will take place, as before.

The following apparatus is necessary to produce the exact reflexion of the beam :—At each station a telescope is directed to aim at the centre of the object-glass of the opposite station. The beam of light is sent through the first telescope : the pencil of rays, rendered nearly parallel, is received by the second and concentrated in its focus, and there reflected by a small mirror. After reflexion, the rays follow exactly the same path, and come back at the very point they start from. The observer can receive these *return rays* without being blinded by the source of light, by interposition of a piece of transparent glass, which reflects a good part of these *return rays*.

M. Fizeau's Experiment (between Suresne and Montmartre) was made to prove that it was possible, not only to establish the duration of the propagation of light, but also to measure its velocity without the intervention of astronomical phenomena. The distance of the stations was 8633^m, about 5½ English miles. The number found by M. Fizeau agreed sufficiently with the astronomical result to give the greatest confidence in the exactness of the method, when applied under fair conditions. A new experiment was arranged with Arago in the Paris Observatory, but Arago's death prevented the execution of this design.

Professor Cornu's Researches.—First experiments were made between the Polytechnic School in Paris and Mont Valerien. (Distance, 10310^m, about 6½ English miles.)

His researches were conducted with a view to improve the method of the toothed wheel, in order to obtain the greatest exactness. The

chief difficulty for the practical application of this method is to measure the angular motion or velocity of the wheel, to which the velocity of light is directly compared. The simplest means would have been, as in M. Fizeau's experiment, to give an uniform motion to the wheel; but such a motion is practically impossible to obtain, so it was necessary to find another mode of measure. The principle of the new improvement was the use of an *electrical registering apparatus*, to register the continuous increase of motion of the wheel. With that arrangement an exact uniform motion is no longer necessary, the observer being able by a peculiar electric signal to point out the instant at which the right velocity is obtained.

The second improvement, and one very important for the exactness of the method, is the substitution of a pair of observations of the return rays, when reduced to a determined feeble intensity, for the single observation of a total extinction.

These improvements, experimentally tried in 1872, gave the velocity of light as 298,000 kilometres per second. The probable error does not rise to 1 per cent.

Professor Fizeau's New Determination was made between the Paris Observatory and the tower of Montlhéry. (Distance, 22910^m, about 14½ English miles.)

A direct determination of the velocity of light was ordered at the beginning of 1874 by the Council of the Paris Observatory, on the proposal of M. Le Verrier, Director, and of M. Fizeau, Councillor. The best conditions were chosen for the optical and mechanical apparatus, and the stations were placed at an increased distance. One was erected upon the higher terrace of the Observatory, and supplied with a telescope of 0.38^m (1½ foot) aperture, and 9^m (30 feet) focal length. The telescope and the remainder of the apparatus (toothed wheel, registering cylinder, clocks, &c.) were sheltered under a large cabin constructed on purpose. The opposite station was erected on the top of the tower of Montlhéry; it contains only a reflexion telescope sheltered by a cast-iron tube.

The experiments were made in the summer of 1874. The average of 508 pairs of observations gave the velocity as 300,400 kilometres in a second of mean time. The probable error appears not to exceed one-thousandth.

Second Solution for Direct Measurement of the Velocity of Light was obtained by the method of the revolving mirror (1850); based on the use of it by Sir Charles Wheatstone in his beautiful researches on the Velocity of Electricity (1834). Arago, after an enthusiastic account of these researches before the Paris Academy, showed how the new apparatus might be adapted to solve some most important problems of optics (1838), and specially to decide between the emission and the undulatory theory of light. He gave (April, 1850) a full description of his own attempts on the subject, but he was not

able, through failing eyesight, to fulfil his design. Some days after, the complete solution of the problem was brought before the Academy simultaneously by Foucault and by MM. Fizeau and Bréguet. Foucault, in the year 1865, improved in several points the revolving mirror method, and obtained a direct determination of the velocity of light (298,000 kilometres).

The principle of the experiment is as follows :—

A beam of light reflected on a revolving mirror is normally reflected by a fixed concave mirror, and comes back again on the revolving one: during the time of the propagation of light from the first mirror to the second and back, the revolving mirror has suffered a little angular motion; the new reflexion on it produces a small deflection on the return beam; from that deflection the velocity of light can be computed.

This method is certainly one of the most curious, but the deflections are so small and the march of the rays takes place in such extraordinary circumstances that it is difficult to ascertain the degree of approximation of the result.

Physical Importance of the Direct Determination of the Velocity of Light.—The importance of the result is perhaps greater for those physicists who occupy themselves with electricity than for those who work on optics. The beautiful experiments and theories of Prof. Maxwell, Sir William Thomson, &c., so clearly expounded by the British Association Electrical Standard Committee, have shown that the velocity of light is a coefficient common to the undulatory waves, and to the mode of motion which is called electricity. Several determinations, but purely electrical ones, have been made in England of that coefficient, and the results agree as well as possible, in that delicate matter, with the above-given value.

Astronomical Importance of the same Determination.—The numbers measuring the phenomena discovered by Roemer and Bradley, combined with the approached distance of the sun to the earth, have a hundred and fifty years ago furnished an approximate value of the velocity of light. Now the progress of science requires an inverse march; the exact value of the velocity of light permits, by the inverted calculus, the computation of the mean distance of the sun or the sun's parallax, that is to say, the same element which is directly given by the transit of Venus. Professor Cornu's last result, combined with Delambre's equation of light (deduced from more than a thousand observations of eclipses of Jupiter's satellites) or of Bradley's aberration value, which seems one of the best determined number, agree exactly with the result obtained by M. Le Verrier in his researches on planetary perturbations, and with the already known results of the last transit of Venus observations.

[A. C.]

NOTES OF PROFESSOR GLADSTONE'S FIFTH LECTURE ON CHEMICAL FORCE.

Tuesday, June 1, 1875.

The Copper-Zinc Couple and its Effects.

IN an ordinary Voltaic cell the liquid is decomposed under the influence of the two different metals in contact, but this decomposition is always impeded more or less by the "resistance" of the liquid; indeed, in the case of very many compounds, especially organic liquids, this internal resistance is so great that practically no Voltaic decomposition is capable of being effected. When the junction of the metals is made outside the cell as in all batteries, there is also more or less external resistance. Now the resistance offered by a badly conducting liquid, such as pure water, depends upon the amount of it that lies between the two metals, and the power is most advantageously applied when the distance is reduced to a minimum, and there is no part of the circuit outside the liquid. This is effected in the copper-zinc couple, which has been recently applied by Professor Gladstone and Mr. A. Tribe in the laboratory of the Institution, and elsewhere, to the decomposition of many compound bodies, and the preparation of several substances hitherto unknown.

If a piece of zinc be immersed in a solution of cupric sulphate, copper is deposited upon it in a minute state of division, and thus the two metals touch at myriads of points. When this "couple" is immersed in a binary liquid, the liquid at each point of junction is exposed to the full chemical or electromotive force of the metals.

In this way pure water may be decomposed with the production of pure hydrogen gas; organic haloid bodies, such as ethylic iodide, and its congeners, may be split up, and thus there may be prepared zinc ethyl, zinc propyl, &c., bodies spontaneously inflammable in the air; the same haloid bodies in the presence of alcohol may be decomposed with the production of the hydrides of the radicals, such as marsh gas, and a new set of compounds the zinc haloid ethylates; chloroform, bromoform, and iodoform may be made to yield the same hydrides, haloid ethylates, and acetylene; while isomeric bodies such as the chlorides of ethylene, and ethylidene, may be examined as to their chemical structure.

The importance of time as an element in chemical action is well illustrated in many of these decompositions; and they are generally greatly facilitated by a rise of temperature, whether that result from the chemical action itself, or from external sources.

The copper-zinc couple has been practically applied to the production of certain organic compounds, and to the determination of nitrates in potable waters.

WORK DONE BY MEANS OF GLADSTONE AND TRIBE'S COPPER-ZINC COUPLE.

Date.	Chief Results.	Chemistry of Operation.
1872	Decomposition of Water, and Preparation of Pure Hydrogen	$\text{ZnCu} + 2\text{H}_2\text{O} = \text{Cu} + \text{Zn}2\text{HO} + \text{H}_2$
1873	Direct Formation of Zinc Ethiodide, and	$\text{ZnCu} + \text{C}_2\text{H}_5\text{I} = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{I} \end{smallmatrix} \right.$
	Preparation of Zinc Ethyl, Ethyl Hydride and Zinc Iodo-ethylate	$2\text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{I} \end{smallmatrix} \right. = \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{C}_2\text{H}_5 \end{smallmatrix} \right. + \text{ZnI}_2$ $\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{H} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{I} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{I} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right.$
1873	Preparation of Di-amyl, ..	$\text{ZnCu} + 2 \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{I} \end{smallmatrix} \right. = \text{Cu} + \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right. + \text{ZnI}_2$
	Zinc-amyl, and Amyl hydride.	$2\text{ZnCu} + 2 \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{I} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{C}_5\text{H}_{11} \end{smallmatrix} \right. + \text{ZnI}_2$ $\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11}\text{O} \\ \text{H} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{I} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11}\text{O} \\ \text{I} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_5\text{H}_{11} \\ \text{H} \end{smallmatrix} \right.$
	Preparation of Methyl Hydride.	$\text{ZnCu} + \text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{I} = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{I} \end{smallmatrix} \right. + \text{CH}_4$
1873	Preparation of Zinc Isopropyl, Zinc prop-iodide, Zinc propyl, and Propyl Hydride	$2\text{ZnCu} + 2 \left\{ \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{I} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{smallmatrix} \right. + \text{ZnI}_2$ $\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{I} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{I} \end{smallmatrix} \right.$ $2\text{Zn} \left\{ \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{I} \end{smallmatrix} \right. = \text{ZnI}_2 + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{C}_3\text{H}_7 \end{smallmatrix} \right.$ $\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_3\text{H}_7 \\ \text{I} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{H} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{I} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right.$
1874	Isolation of Di-allyl, and ..	$\text{ZnCu} + 2 \left\{ \begin{smallmatrix} \text{C}_3\text{H}_5 \\ \text{I} \end{smallmatrix} \right. = \text{Cu} + \left\{ \begin{smallmatrix} \text{C}_3\text{H}_5 \\ \text{C}_3\text{H}_5 \end{smallmatrix} \right. + \text{ZnI}_2$
	Preparation of Pure Propylene.	$\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_3\text{H}_5 \\ \text{I} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{H} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{I} \end{smallmatrix} \right. + \text{C}_2\text{H}_4$
1874	Preparation of Pure Olefant Gas and its homologues ..	$\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_n\text{H}_{2n} \\ \text{Br}_2 \end{smallmatrix} \right. = \text{Cu} + \text{ZnBr}_2 + \text{C}_n\text{H}_{2n}$
1874	Preparation of Zinc Ethylobro- mide, and	$\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{Br} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{Br} \end{smallmatrix} \right.$
	Zinc Brom-ethylate	$\text{ZnCu} + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{Br} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{H} \end{smallmatrix} \right. = \text{Cu} + \text{Zn} \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5\text{O} \\ \text{Br} \end{smallmatrix} \right. + \left\{ \begin{smallmatrix} \text{C}_2\text{H}_5 \\ \text{H} \end{smallmatrix} \right.$

Date.	Chief Results.	Chemistry of Operation.
1874	Preparation of Zinc Chloroethylene, and direct Hydrogenization of Ethylidene	$2\text{ZnCu} + \left\{ \begin{array}{l} \text{C}_2\text{H}_4\text{Cl} \\ \text{Cl} \end{array} \right\} + 2\left\{ \begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \right\} = \text{Cu} + 2\text{Zn}\left\{ \begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{Cl} \end{array} \right\} + \left\{ \begin{array}{l} \text{C}_2\text{H}_3 \\ \text{H} \end{array} \right\}$
1875	Complete Hydrogenization of Chloroform, and	$3\text{ZnCu} + \text{CHCl}_3 + 3\left\{ \begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{H} \end{array} \right\} = \text{Cu} + 3\text{Zn}\left\{ \begin{array}{l} \text{C}_2\text{H}_3\text{O} \\ \text{Cl} \end{array} \right\} + \text{CH}_4$
	Its homologues and preparation of Acetylene	$3\text{ZnCu} + 2\text{CHI}_3 = \text{Cu} + 3\text{ZnI}_2 + \text{C}_2\text{H}_2$
(Investigated by Prof. Thorpe.)		
1873	Conversion of Nitrates into Ammonia	$4\text{ZnCu} + 6\text{H}_2\text{O} + \text{KNO}_3 = \text{Cu} + 4\text{ZnH}_2\text{O}_2 + \text{KHIO} + \text{NH}_3$

The new substances discovered during these investigations are in italics.

Cu signifies simply the metal copper, and not an atomic proportion.

Friday, February 11, 1876.

THE HON. SIR WILLIAM ROBERT GROVE, M.A. Ph.D. F.R.S.

Just. C. P., Manager, in the Chair.

W. CROOKES, Esq. F.R.S.

The Mechanical Action of Light.

To generate motion has been found a characteristic common, with one exception, to all the phases of physical force. We hold the bulb of a thermometer in our hands, and the mercury expands in bulk, and, rising along the scale, indicates the increase of heat it has received. We heat water, and it is converted into steam, and moves our machinery, our carriages, and our ironclads. We bring a loadstone near a number of iron filings, and they move towards it, arranging themselves in peculiar and intricate lines; or we bring a piece of iron near a magnetic needle, and we find it turned away from its ordinary position. We rub a piece of glass with silk, thus throwing it into a state of electrical excitement, and we find that bits of paper or thread fly towards it, and are, in a few moments, repelled again. If we remove the supports from a mass of matter it falls, the influence of gravitation being here most plainly expressed in motion, as shown in clocks and water-mills. If we fix pieces of paper upon a stretched string, and then sound a musical note near it, we find certain of the papers projected from their places. Latterly, the so-called "sensitive flames," which are violently agitated by certain musical notes, have become well known as instances of the conversion of sound into motion. How readily chemical force undergoes the same transformation is manifested in such catastrophes as those of Bremerhaven, in the recent deplorable coal-mine explosions, and indeed in every discharge of a gun.

But light, in some respects the highest of the powers of nature, has not been hitherto found capable of direct conversion into motion, and such an exception cannot but be regarded as a singular anomaly.

This anomaly the researches which I am about to bring before you have now removed; and, like the other forms of force, light is found to be capable of direct conversion into motion, and of being—like heat, electricity, magnetism, sound, gravitation, and chemical

action—most delicately and accurately measured by the amount of motion thus produced.

My research arose from the study of an anomaly.

It is well known to scientific men that bodies appear to weigh less when they are hot than when they are cold; the explanation given being, that the ascending currents of hot air buoy up the body, so to speak. Wishing to get rid of this and other interfering actions of the air during a research on the atomic weight of thallium, I had a balance constructed in which I could weigh in a vacuum. I still, indeed, found my apparatus less heavy when hot than when cold. The obvious explanations were evidently not the true ones: *obvious* explanations seldom are true ones, for simplicity is not a characteristic of nature.

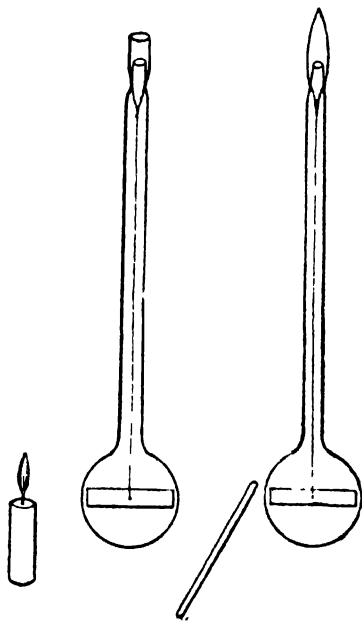
An unknown disturbing cause was interfering, and the endeavour to find the clue to the apparent anomaly has led to the discovery of the mechanical action of light.

I was long troubled by the apparent lawlessness of the actions I obtained. By gradually increasing the delicacy of my apparatus I could easily get certain results of motion when hot bodies were brought near them, but sometimes it was one of attraction, at others of repulsion, whilst occasionally no movement whatever was produced.

I will try to reproduce these phenomena in this apparatus (Fig. 1). Here are two glass bulbs, each containing a bar of pith about 3 inches long and half an inch thick, suspended horizontally by a long fibre of cocoon silk. I bring a hot glass rod, or a candle, towards one of them, and you see that the pith is gradually attracted, following the candle as I move it round the bulb. That seems a very definite fact; but look at the action in the other bulb. I bring the candle, or a hot glass rod, near the other bar of pith, and it is strongly *repelled* by it—much more strongly than it was attracted in the first instance.

Here, again, is a third fact. I bring a piece of ice near the pith bar which has just been repelled by the hot rod, and it is attracted, and follows the rod round as a magnetic needle follows a piece of iron.

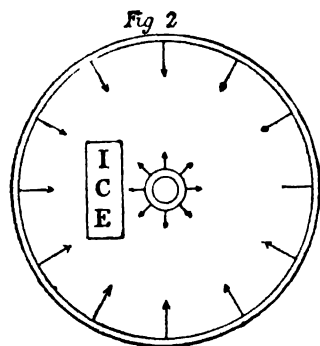
FIG. 1.



The repulsion by radiation is the key-note of these researches. The movement of a small bar of pith is not very distinct, except to those near, and I wish to make this repulsion evident to all. I have therefore arranged a piece of apparatus by which it can be seen by all present. I will, by means of the electric light, project an image of a pendulum suspended *in vacuo* on the screen. You see that the approach of a candle gives the bob a veritable push, and, by alternately obscuring and uncovering the light, I can make the pendulum beat time to my movements.

What then is the cause of the contradictory action in these two bulbs—attraction in one, and repulsion in the other? It can be explained in a few words. Attraction takes place when air is present, and repulsion when air is absent.

Neutrality, or no movement, is produced when the vacuum is insufficient. A minute trace of air in the apparatus interferes most materially with the repulsion, and for a long time I was unaware of the powerful action produced by radiation in a "perfect" vacuum.



It is not at first sight obvious how ice or a cold body can produce the opposite effect to heat. The law of exchanges, however, explains this perfectly. The pith bar and the whole of the surrounding bodies are incessantly exchanging heat-rays; and under ordinary circumstances the income and expenditure of heat are in equilibrium. Let me draw your attention to the diagram (Fig. 2) illustrating what takes place when I bring a piece of ice near the apparatus. The centre circle represents

my piece of pith; the arrows show the influx and efflux of heat. A piece of ice brought near cuts off the influx of heat from one side, and therefore allows an excess of heat to fall on the pith from the opposite side. Attraction by a cold body is therefore seen to be only repulsion by the radiation from the opposite side of the room.

The later developments of this research have demanded the utmost refinement of apparatus. Everything has to be conducted in glass vessels, and these must be blown together till they make one piece, for none but fused joints are admissible. In an investigation depending for its successful prosecution on manipulative dexterity, I have been fortunate in having the assistance of my friend Mr. Charles Gimingham. All the apparatus you see before you are the fruits of his skilful manipulation, and I now want to draw your attention to what I think is a masterpiece of glass-working—the pump which enables me so readily to produce a vacuum unattainable by ordinary means.

The pump here at work is a modification of the Sprengel pump, but it contains two or three valuable improvements. I cannot attempt to describe the whole of the arrangements, but I will rapidly run over them as illuminated by the electric light. It has a triple fall tube in which the mercury is carried down, thus exhausting with threefold rapidity; it has Dr. McCleod's beautiful arrangement for measuring the residual gas; it has gauges in all directions, and a small radiometer attached to it to tell the amount of exhaustion that I get in any experiments; it has a contrivance for admitting oil of vitriol into the tubes without interfering with the progress of the exhaustion, and it is provided with a whole series of most ingenious vacuum-taps devised by Mr. Giningham. The exhaustion produced in this pump is such that a current of electricity from an induction-coil will not pass across the vacuum. This pump is now exhausting a torsion balance, which will be described presently. Another pump, of a similar kind but less complicated, is exhausting an apparatus which has enabled me to pass from the mere exhibition of the phenomena to the obtaining of quantitative measurements.

A certain amount of force is exerted when a ray of light or heat falls on the suspended pith, and I wished to ascertain—

First. What were the actual rays—invisible heat, luminous, or ultra-violet—which caused this action?

Secondly. What influence had the colour of the surface on the action?

Thirdly. Was the amount of action in direct proportion to the amount of radiation?

Fourthly. What was the amount of force exerted by radiation?

I required an apparatus which would be easily moved by the impact of light on it, but which would readily return to zero, so that measurements might be obtained of the force exerted when different amounts of light acted on it. At first I made an apparatus on the Zollner's horizontal pendulum. For a reason that will be explained presently, I am unable to show you the apparatus at work, but the principle of it is shown in the diagram (Fig. 3). The pendulum represented by this horizontal line has a weight at the end. It is supported on two fibres of glass, one stretched upwards and the other stretched downwards, both firmly fastened at the ends, and also attached to the horizontal rod (as shown in the figure) at points near together, but not quite opposite to one another.

It is evident that if there is a certain amount of pull upon each of these fibres, and that the pull can be so adjusted as to counteract the weight at the end and keep it horizontal, the nearer the beam approaches the horizontal line the slower its rate of oscillation. If I relax the tension, by throwing the horizontal beam downwards, I get a more rapid oscillation sideways. If I turn the levelling screw so as to raise the beam and weight, the nearer it approaches the horizontal position the slower the oscillation becomes, and the more delicate is

the instrument. Here is the actual apparatus that I tried to work with. The weight at the end is a piece of pith; in the centre is a glass mirror, on which to throw a ray of light, so as to enable me to see the movements by a luminous index. The instrument, enclosed in glass and exhausted of air, was mounted on a stand with levelling screws, and with it I tried the action of a ray of light falling on the pith. I found that I could get any amount of sensitiveness that I liked; but it was not only sensitive to the impact of a ray of light, it was immeasurably more so to a change of horizontality. It was, in fact, too delicate for me to work with. The slightest elevation of one end of the instrument altered the sensitiveness, or the position of the

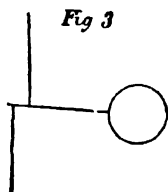


Fig 3

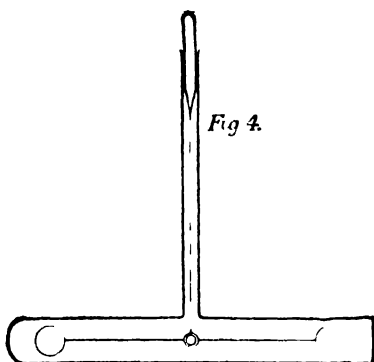


Fig 4.

zero-point, to such a degree that it was impossible to try any experiments with it in such a place as London. A person stepping from one room to another altered the position of the centre of gravity of the house. If I walked from one side of my own laboratory to the other, I tilted the house over sufficiently to upset the equilibrium of the apparatus. Children playing in the streets disturbed it. Professor Rood, who has worked with an apparatus of this kind in America, finds that an elevation of its side equal to $\frac{1}{1000000}$ part of an inch is sufficient to be shown on the instrument. It was therefore out of the question to use an instrument of this construction, so I tried another form (shown in Fig. 4), in which a fine glass beam, having discs of pith at each end, is suspended horizontally by a fine glass fibre, the whole being sealed up in glass and perfectly exhausted. To the centre of oscillation a glass mirror is attached.

Now a glass fibre has the property of always coming back to zero when it is twisted out of its position. It is almost, if not quite, a perfectly elastic body. I will show this by a simple experiment. This is a long glass fibre hanging vertically, and having a horizontal bar suspended on it. I hold the bar, and turn it half round; it swings backwards and forwards for a few times, but it quickly comes back to

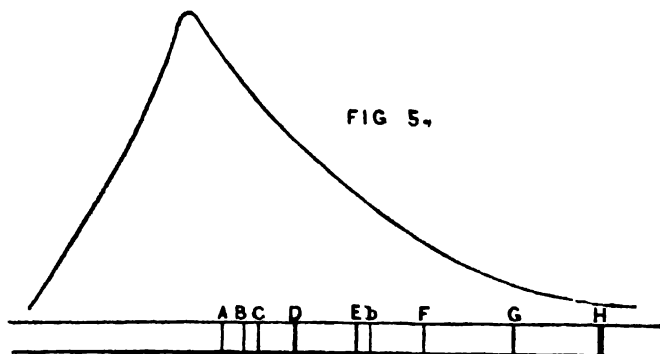
its original position. However much twist, however much torsion, may be put on this, it always returns ultimately to the same position. I have twisted glass fibres round, and kept them in a permanent state of twist more than a hundred complete revolutions, and they always came back accurately to zero. The principle of an instrument that I shall describe farther on depends entirely on this property of glass.

Instead of using silk to suspend the torsion beam with, I employ a fibre of glass, drawn out very fine before the blowpipe. A thread of glass of less than the thousandth of an inch in thickness is wonderfully strong, of great stiffness, and of perfect elasticity, so that however much it is twisted round short of the breaking point, it untwists itself perfectly when liberated. The advantage of using glass fibres for suspending my beam is, therefore, that it always returns accurately to zero, after having tried an experiment, whilst I can get any desired amount of sensitiveness by drawing out the glass fibre sufficiently fine.

Here, then, is the torsion apparatus sealed on to a Sprengel pump. You will easily understand the construction by reference to the diagram (Fig. 4). It consists of a horizontal beam suspended by a glass fibre, and having discs of pith at each end coated with lamp-black. The whole is enclosed in a glass case, made of tubes blown together, and by means of the pump the air is entirely removed. In the centre of the horizontal beam is a silvered mirror, and a ray from the electric light is reflected from it on to a scale in front, where it is visible as a small circular spot of light. It is evident that an angular movement of the torsion beam will cause the spot of light to move to the right or to the left along the scale. I will first show you the wonderful sensitiveness of the apparatus. I simply place my finger near the pith disc at one end, and the warmth is quite sufficient to drive the spot of light several inches along the scale. It has now returned to zero, and I place a candle near it. The spot of light flies off the scale. I now bring the candle near it alternately from one side to the other, and you see how perfectly it obeys the force of the candle. I think the movement is almost better seen without the screen than with it. The fog, which has been so great a detriment to everyone else, is rather in my favour, for it shows the luminous index like a solid bar of light swaying to and fro across the room. The warmth of my finger, or the radiation from a candle, is therefore seen to drive the pith disc away. Here is a lump of ice, and on bringing it near one of the discs the luminous index promptly shows a movement of apparent attraction.

With this apparatus I have tried many experiments, and amongst others I have endeavoured to answer the question, "Is it light, or is it heat, that produces the movement?" for that is a question that is asked me by almost everyone; and a good many appear to think that if the motion can be explained by an action of heat, all the novelty and the importance of the discovery vanish. Now this question of light or heat is one I cannot answer, and I think that when I have explained the reason you will agree with me that it is unanswerable.

There is no physical difference between light and heat. Here is a diagram of the visible spectrum (Fig. 5). The spectrum, as scientific men understand it, extends from an indefinite distance beyond the red



to an indefinite distance beyond the violet. We do not know how far it would extend one way or the other if no absorbing media were present; but, by what we may call a physiological accident, the human eye is sensitive to a portion of the spectrum situated between the line A in the red to about the line H in the violet. But this is not a physical difference between the luminous and non-luminous parts of the spectrum; it is only a physiological difference. Now, the part at the red end of the spectrum possesses, in the greatest degree, the property of causing the sensation of warmth, and of dilating the mercury in a thermometer, and of doing other things which are conveniently classed among the effects of *heat*; the centre part affects the eye, and is therefore called *light*; whilst the part at the other end of the spectrum has the greatest energy in producing *chemical action*. But it must not be forgotten that any ray of the spectrum, from whatever part it is selected, will produce all these physical actions in more or less degree. A ray here, at the letter C for instance in the orange, if concentrated on the bulb of a thermometer, will cause the mercury to dilate, and thus show the presence of *heat*; if concentrated on my hand I feel *warmth*; if I throw it on the face of a thermo-pile it will produce a current of *electricity*; if I throw it upon a sensitive photographic plate it will produce *chemical action*; and if I throw it upon the instrument I have just described, it will produce *motion*. What, then, am I to call that ray? Is it light, heat, electricity, chemical action, or motion? It is neither. All these actions are inseparable attributes of the ray of that particular wave-length, and are not evidences of separate identities. I can no more split that ray up into five or six different rays each having different properties, than I can split up the element iron, for instance, into other elements, one possessing the specific gravity of iron, another its magnetic

properties, a third its chemical properties, a fourth its conducting power for heat, and so on. A ray of light of a definite refrangibility is one and indivisible, just as an element is, and these different properties of the ray are mere functions of that refrangibility, and inseparable from it. Therefore when I tell you that a ray in the ultra-red pushes the instrument with a force of 100, and a ray in the most luminous part has a dynamic value of about half that, it must be understood that the latter action is not due to heat-rays which accompany the luminous rays, but that the action is one purely due to the wave-length and the refrangibility of the ray employed. You now understand why it is that I cannot give a definite answer to the question, "Is it heat or is it light that produces these movements?" There is no physical difference between heat and light; so, to avoid confusion, I call the total bundle of rays which come from a candle or the sun, *radiation*.

I found, by throwing the pure rays of the spectrum one after the other upon this apparatus, that I could obtain a very definite answer to my first question, "What are the actual rays which cause this action?"

The apparatus was fitted up in a room specially devoted to it, and was protected on all sides, except where the rays of light had to pass, with cotton-wool and large bottles of water. A heliostat reflected a beam of sunlight in a constant direction, and it was received on an appropriate arrangement of slit, lenses, prisms, &c., for projecting a pure spectrum. Results were obtained in the months of July, August, and September; and they are given in the figure (Fig. 5) graphically as a curve, the maximum being in the ultra-red and the minimum in the ultra-violet. Taking the maximum at 100, the following are the mechanical values of the different colours of the spectrum:

Ultra-red	100
Extremc red	85
Red	73
Orange	66
Yellow	57
Green	41
Blue	22
Indigo	8½
Violet	6
Ultra-violet	5

A comparison of these figures is a sufficient proof that the mechanical action of radiation is as much a function of the luminous rays as it is of the dark heat-rays.

The second question, namely, "What influence has the colour of the surface on the action?" has also been solved by this apparatus.

In order to obtain comparative results between discs of pith coated with lampblack and with other substances, another torsion apparatus was constructed, in which six discs *in vacuo* could be exposed one after

the other to a standard light. One disc always being lampblacked pith, the other discs could be changed so as to get comparisons of action. Calling the action of radiation from a candle on the lampblacked disc 100, the following are the proportions obtained :

Lampblacked pith	100
Iodide of palladium	87·3
Precipitated silver	56
Amorphous phosphorus	40
Sulphate of baryta	37
Milk of sulphur	31
Red oxide of iron	28
Scarlet iodide of mercury and copper	22
Lampblacked silver	18
White pith	18
Carbonate of lead	13
Rock-salt	6·5
Glass	6·5

This table gives important information on many points: one more especially—the action of radiation on lampblacked pith is $5\frac{1}{2}$ times what it is on plain pith. A bar like those used in my first experiment, having one half black and one half white, exposed to a broad beam of radiation, will be pushed with $5\frac{1}{2}$ times more strength on the black than on the white half, and if freely suspended will set at an angle greater or less according to the intensity of the radiation falling on it.

This suggests the employment of such a bar as a photometer, and I have accordingly made an instrument on this principle: its construction is shown in the diagram (Fig. 6). It consists of a flat bar of pith, A, half black and half white, suspended horizontally in a bulb by means of a long silk fibre. A reflecting mirror, B, and small magnet, C, are fastened to the pith, and a controlling magnet, D, is fastened outside, so that it can slip up and down the tube, and thus increase or diminish sensitiveness. The whole is completely exhausted and then enclosed in a box lined with black velvet, with apertures for the rays of light to pass in and out. A ray of light from a lamp, F, reflected from the mirror, B, to a graduated scale, G, shows the movements of the pith bar.

The instrument fitted up for a photometric experiment is in front of me on the table. A beam from the electric light falls on the little mirror, and is thence reflected back to the screen, where it forms a spot of light, the displacement of which to the right or the left shows the movement of the pith bar. One end of the bar is blacked on each side, the other end being left plain. I have two candles, E E, each 12 inches off the pith bar, one on each side of it. When I remove the screens, H H, the candle on one side will give the pith a push in one direction, and the candle on the other side will give the pith a push in the opposite direction, and as they are the same distance off they will neutralize each other, and the spot of light will not move. I now take the two screens away; each candle is pushing the pith equally

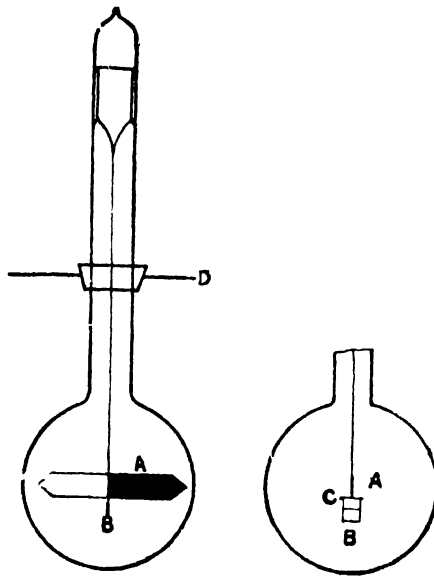
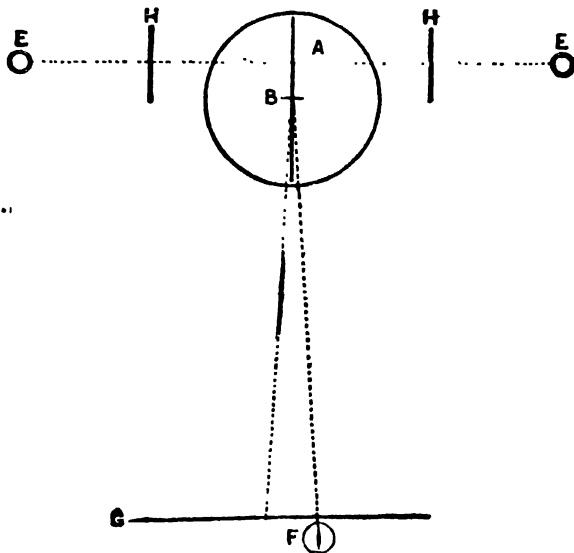


FIG. 6.,



in opposite directions, and the luminous index remains at zero. When, however, I cut one candle off, the candle on the opposite side exerts its full influence, and the index flies to one end of the scale. I cut the other one off and obscure the first, and the spot of light flies to the other side. I obscure them both, and the index comes quickly to zero. I remove the screens simultaneously, and the index does not move.

I will retain one candle 12 inches off, and put two candles on the other side 17 inches off. On removing the screens you see the index does not move from zero. Now the square of 12 is 144, and the square of 17 is 289. Twice 144 is 288. The light of these candles, therefore, is as 288 to 289. They therefore balance each other as nearly as possible. Similarly I can balance a gas-light against a candle. I have a small gas-burner here, which I place 28 inches off on one side, and you see it balances the candle 12 inches off. These experiments show how conveniently and accurately this instrument can be used as a photometer. By balancing a standard candle on one side against any source of light on the other, the value of the latter in terms of a candle is readily shown; thus in the last experiment the standard candle 12 inches off is balanced by a gas-flame 28 inches off. The lights are therefore in the proportion of 12^2 to 28^2 , or as 1 to 5.4. The gas-burner is therefore equal to about $5\frac{1}{2}$ candles.

In practical work on photometry it is often required to ascertain the value of gas. Gas is spoken of commercially as of so many candle-power. There is a certain "standard" candle which is supposed to be made invariable by Act of Parliament. I have worked a great deal with these standard candles, and I find them to be among the most variable things in the world. They never burn with the same luminosity from one hour to the other, and no two candles are alike. I can now, however, easily get over this difficulty. I place a "standard" candle at such a distance from the apparatus that it gives a deflection of 100 degrees on the scale. If it is poorer than the standard, I bring it nearer; if better, I put it farther off. Indeed, any candle may be taken; and if it be placed at such a distance from the apparatus that it will give a uniform deflection, say of 100 divisions, the standard can be reproduced at any subsequent time; and the burning of the candle may be tested during the photometric experiments by taking the deflection it causes from time to time, and altering its distance, if needed, to keep the deflection at 100 divisions. The gas-light to be tested is placed at such a distance on the opposite side of the pith bar that it exactly balances the candle. Then, by squaring the distances, I get the exact proportion between the gas and the candle.

Before this instrument can be used as a photometer or light measurer, means must be taken to cut off from it all those rays coming from the candle or gas which are not actually luminous. A reference to the spectrum diagram (Fig. 5) will show that at each end of the coloured rays there is a large space inactive, as far as the eye is con-

cerned, but active in respect to the production of motion—strongly so at the red end, less strong at the violet end. Before the instrument can be used to measure luminosity, these rays must be cut off. We buy gas for the light that it gives, not for the heat it evolves on burning, and it would therefore never do to measure the heat and pay for it as light.

It has been found that a clear plate of alum, whilst letting all the light through, is almost, if not quite, opaque to the heating rays below the red. A solution of alum in water is almost as effective as a crystal of alum; if, therefore, I place in front of the instrument glass cells containing an aqueous solution of alum, the dark heat-rays are filtered off.

But the ultra-violet rays still pass through, and to cut these off I dissolve in the alum solution a quantity of sulphate of quinine. This body has the property of cutting off the ultra-violet rays from a point between the lines G and H. A combination of alum and sulphate of quinine, therefore, limits the action to those rays which affect the human eye, and the instrument, such as you see it before you, becomes a true photometer.

This instrument, when its sensitiveness is not deadened by the powerful control magnet I am obliged to keep near it for these experiments, is wonderfully sensible to light. In my own laboratory a candle 36 feet off produces a decided movement, and the motion of the index increases inversely with the square of the distance, thus answering the third question, "Is the amount of action in direct proportion to the amount of radiation?"

The experimental observations and the numbers which are required by the theoretical diminution of light with the square of the distance, are sufficiently close, as the following figures show :

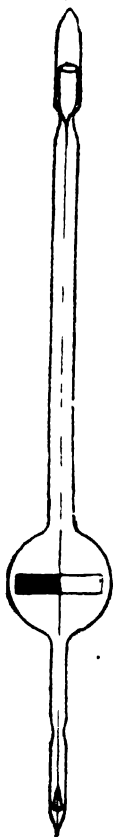
Candle	6 feet off	gives a deflection of	218·0°
"	12	"	54·0°
"	18	"	24·5°
"	24	"	13·0°
"	10	"	77·0°
"	20	"	19·0°
"	30	"	8·5°

The effect of two candles side by side is practically double, and of three candles three times that of one candle.

In the instrument just described the candle acts on a pith bar, one end of which is blacked on each side. But suppose I black the bar on alternate halves and place a light near it sufficiently strong to drive the bar half round. The light will now have presented to it another black surface in the same position as the first, and the bar will be again driven in the same direction half round. This action will be again repeated, the differential action of the light on the black and white surfaces keeps the bar moving, and the result will be rotation.

Here is such a pith bar, blacked on alternate sides, and suspended in an exhausted glass bulb (Fig. 7). I project its image on the screen, and the strong light which shines on it sets it rotating with considerable velocity. Now it is slackening speed, and now it has

FIG. 7



stopped altogether. The bar is supported on a fibre of silk, which has twisted round till the rotation is stopped by the accumulated torsion. I put a water screen between the bar and the electric light to cut off some of the active rays, and the silk untwists, turning the bar in the opposite direction. I now remove the water, and the bar revolves rapidly as at first.

From suspending the pith on a silk fibre to balancing it on a point the transition is slight; the interfering action of torsion is thereby removed, and the instrument rotates continuously under the influence of radiation. Many of these little pieces of apparatus, to which I have given the name of radiometers, are on the table, revolving with more or less speed. The diagram (Fig. 8) shows their construction, which is very simple. They are formed of four arms of very fine glass, supported in the centre by a needle-point, and having at the extremities thin discs of pith lamp-blackened on one side, the black surfaces all facing the same way. The needle stands in a glass cup, and the arms and discs are delicately balanced so as to revolve with the slightest impetus.

Here are some rotating by the light of a candle. This one is now rather an historical instrument, being the first one in which I saw rotation. It goes very slowly in comparison with the others, but it is not bad for the first instrument of the sort that was ever made.

I will now, by means of a vertical lantern, throw on the screen the projection of one of these instruments, so as to show the movement rather better than you could see it on the table. The electric light falling vertically downwards on it, and much of the power being cut off by water and alum screens, the rotation is slow. I bring a candle near and the speed increases. I now lift the radiometer up, and place it full in the electric light, projecting its image direct

on the screen, and it goes so rapidly that if I had not cut out the four pieces of pith of different shapes you would have been unable to follow the movement.

The speed with which a sensitive radiometer will revolve in the sun is almost incredible; and the electric light such as I have in this lantern cannot be far short of full sunshine. Here is the most sensitive instrument I have yet made, and I project its image on the screen, letting the full blaze of the electric light shine upon it.

Nothing is seen but an undefined nebulous ring, which becomes at times almost invisible. The number of revolutions per second cannot be counted, but they must be several hundreds, for one candle has made it spin round forty times a second.

I have called the instrument the radiometer, because it will enable me to measure the intensity of radiation falling on it by counting the revolutions in a given time; the law being that the rapidity of revolution is inversely as the square of the distance between the light and the instrument.

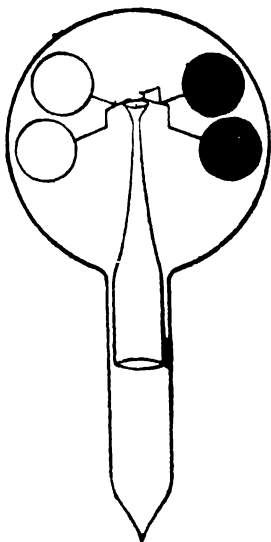
When exposed to different numbers of candles at the same distance off, the speed of revolution in a given time is in proportion to the number of candles; two candles giving twice the rapidity of one candle, and three, three times, &c.

The position of the light in the horizontal plane of the instrument is of no consequence, provided the distance is not altered; thus two candles, 1 foot off, give the same number of revolutions per second, whether they are side by side or opposite to each other. From this it follows that if the radiometer is brought into a uniformly lighted space it will continue to revolve.

It is easy to get rotation in a radiometer without having the surfaces of the discs differently coloured. Here is one having the pith discs blacked on both sides. I project its image on the screen, and there is no movement. I bring a candle near it, and shade the light from one side, when rapid rotation is produced, which is at once altered in direction by moving the shade to the other side.

I have arranged here a radiometer so that it can be made to move by a very faint light, and at the same time its rotation is easily followed by all present. In this bulb is a large six-armed radiometer carrying a mirror in its centre. The mirror is almost horizontal, but not quite so, and therefore when I throw a beam of electric light vertically downwards on to the central mirror, the light is reflected off at a slight angle, and as the instrument rotates its movement is shown by the spot of light travelling round the ceiling in a circle. Here again the fog helps us, for it gives us an imponderable beam of light moving round the room like a solid body, and saving you the trouble of looking up to the ceiling. I now set the radiometer moving round by the light of a candle, and I want to show you that coloured light does not very much interfere with the movement. I place yellow glass in front, and the movement is scarcely diminished

FIG 8



at all. Very deep coloured glass, you see, diminishes it a little more. Blue and green glass make it go a little slower, but still do not diminish the speed one-half. I now place a screen of water in front: the instrument moves with diminished velocity, rotating with about one-fourth its original speed.

Taking the action produced by a candle flame as					100
Yellow glass reduces it to	89
Red	"	"	"	..	71
Blue	"	"	"	..	56
Green	"	"	"	..	56
Water	"	"	"	..	26
Alum	"	"	"	..	15

I now move the candle a little distance off, so as to make the instrument move slower, and bring a flask of boiling water close to it. See what happens. The luminous index no longer moves steadily, but in jerks. Each disc appears to come up to the boiling water with difficulty, and to hurry past it. More and more sluggishly do they move past, until now one has failed to get by, and the luminous beam, after oscillating to and fro a few times, comes to rest. I now gradually bring the candle near. The index shows no movement. Nearer still. There is now a commencement of motion, as if the radiometer was trying to push past the resistance offered by the hot water; but it is not until I have brought the candle to within a few inches of the glass globe that rotation is recommenced. On these pith radiometers the action of dark heat is to repel the black and white surfaces almost equally, and this repulsion is so energetic as to overcome the rotation caused by the candle, and to stop the instrument.

With a radiometer constructed of a good conductor of heat, such as metal, the action of dark heat is different. Here is one made of silvered copper, polished on one side and lampblackened on the other. I have set it moving with a candle slightly the normal way. Here is a glass shade heated so that it feels decidedly warm to the hand. I cover the radiometer with it, and the rotation first stops, and then recommences the reverse way. On removing the hot shade the reverse movement ceases, and normal rotation recommences.

If, however, I place a hot glass shade over a pith radiometer the arms at once revolve the normal way, as if I had exposed the instrument to light. The diametrically opposite behaviour of a pith and a metal instrument when exposed to the dark heat radiated from a hot glass shade is very striking. The explanation of the action is not easy, but it depends on the fact that the metal is one of the best conductors of heat, whilst pith is one of the worst.

One more experiment with this metallic radiometer. I heat it strongly with a spirit lamp, and the arms spin round rapidly. Now the whole bulb is hot, and I remove the lamp: see what happens. The rotation quickly diminishes. Now it is at rest; and now it is

spinning round just as fast the reverse way. I can procure this reverse movement only with difficulty with a pith instrument. The action is due to the metal being a good conductor of heat. As it absorbs heat it moves one way; as it radiates heat it moves the opposite way.

At first I made these instruments of the very lightest material possible, some of them not weighing more than half a grain; and where extreme sensitiveness is required lightness is essential. But the force which carries them round is quite strong enough to move a much greater weight. Thus the metallic instrument I have just experimented with weighs over 13 grains, and here is one still heavier, made of four pieces of looking-glass blacked on the silvered side, which are quickly sent round by the impact of this imponderable agent, and flash the rays of light all round the room when the electric lamp is turned on the instrument.

Before dismissing this instrument, let me show one more experiment. I place the looking-glass and the metal radiometer side by side, and, screening the light from them, they come almost to rest. Their temperature is the same as that of the room. What will happen if I suddenly chill them? I pour a few drops of ether on each of the bulbs. Both instruments begin to revolve. But notice the difference. Whilst the movement in the case of the metal radiometer is direct, that of the looking-glass instrument is reverse. And yet to a candle they both rotate the same way, the black being repelled.

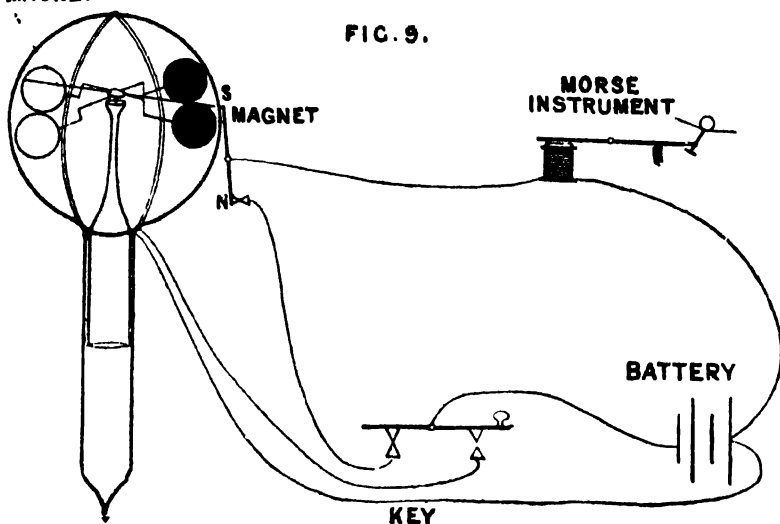
Now, having found that this force would carry round a comparatively heavy weight, another useful application suggested itself. If I can carry round heavy mirrors or plates of copper, I can carry round a magnet. Here, then (Fig. 9), is an instrument carrying a magnet, and outside is a smaller magnet, delicately balanced in a vertical position, having the south pole at the top and the north pole at the bottom. As the inside magnet comes round, the outside magnet, being delicately suspended on its centre, bows backwards and forwards, and, making contact at the bottom, carries an electric current from a battery to a Morse instrument. A ribbon of paper is drawn through the "Morse" by clockwork, and at each contact—at each revolution of the radiometer—a record is printed on the strip of paper by dots; close together if the radiometer revolves quickly, farther apart if it goes slower.

Here the inner magnet is too strong to allow the radiometer to start with a faint light without some initial impetus. Imagine the instrument to be on the top of a mountain away from everybody, and I wish to start it in the morning. Outside the bulb are a few coils of insulated copper wire, and by depressing the key for an instant I pass an electric current from the battery through them. The interior magnet is immediately deflected from its north-south position, and the impetus thus gained enables the light to keep up the rotation. In a proper meteorological instrument I should have an astatic combination inside the bulb, so that a very faint light would be sufficient to start

it, but in this case I am obliged to set it going by an electric current. I have placed a candle near the magnetic radiometer. I now touch the key; the instrument immediately responds; the paper unwinds

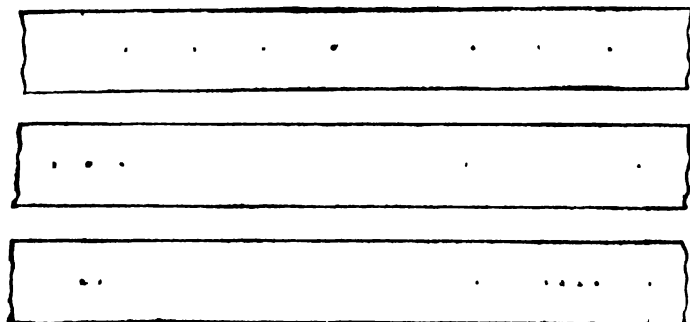
MAGNET

FIG. 9.



from the Morse instrument, and on it you will see dots in regular order. I put the candle 8 inches off, and the dots come wide apart. I place it $5\frac{1}{2}$ inches off, and two dots come where one did before. I bring the candle 4 inches from the instrument, and the dots become

FIG. 10.



four times as numerous (Fig. 10), thus recording automatically the intensity of the light falling on the instrument, and proving that in this case also the radiometer obeys the law of inverse squares.

This instrument, the principle of which I have illustrated to-night, is not a mere toy or scientific curiosity, but is capable of giving much useful information in climatology. You are well aware that the temperature, the rainfall, the atmospheric pressure, the direction and force of the wind, are now carefully studied in most countries, in order to elucidate their sanitary condition, their animal and vegetable productions, and their agricultural capabilities. But one most important element, the amount of light received at any given place, has been hitherto but very crudely and approximately estimated, or rather guessed at. Yet it cannot be denied that sunlight has its effect upon life and health, vegetable, animal, and human, and that its relative amount at any place is hence a point of no small moment. The difficulty is now overcome by such an instrument as this. The radiometer may be permanently placed on some tall building, or high mountain, and, by connecting it by telegraphic wires to a central observatory, an exact account can be kept of the proportion of sunlight received in different latitudes, and at various heights above the sea level. Furthermore, our records of the comparative temperature of different places have been hitherto deficient. The temperature of a country depends partly on the amount of rays which it receives direct from the sun, and partly on the atmospheric and oceanic currents, warm or cold, which sweep over or near it. The thermometer does not discriminate between these influences; but the radiometer will enable us now to distinguish how much of the annual temperature of a place is due to the direct influence of the sun alone, and how much to the other factors above referred to.

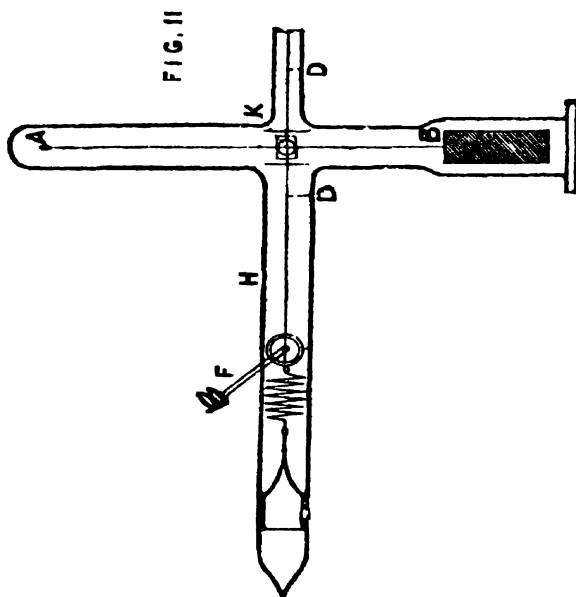
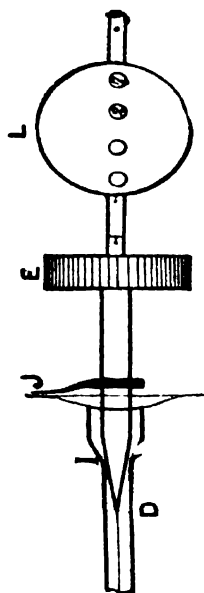
I now come to the last question which I stated at the beginning of this discourse, "What is the amount of force exerted by radiation?" Well, I can calculate out the force in a certain way, from data supplied by this torsion apparatus (Fig. 4). Knowing the weight of the beam, the power of the torsion fibre of glass, its time of oscillation, and the size of the surface acted on, it is not difficult to calculate the amount of force required to deflect the beam through a given angle; but I want to get a more direct measure of the force. I throw a ray of light upon one of these instruments, and it gives a push; surely it is possible to measure the amount of this push in parts of a grain. This I have succeeded in doing in the instrument behind me; but before showing the experiment I want to illustrate the principle upon which it depends. Here is a very fine glass fibre suspended from a horizontal bar, and I wish to show you the strength of it. The fibre is only a few thousandths of an inch thick; it is about 3 feet long, and at the lower end is hanging a scale-pan, weighing 100 grains. So I start with a pull of 100 grains on it. I now add little lead weights, 50 grains each, till it breaks. It bears a pull of 750 grains, but gives way when additional weight is added. You see then the great strength of a fibre of glass, so fine as to be invisible to all who are not close to it, to resist a tensile strain.

Now I will illustrate another equally important property of a glass

thread, viz. its power to resist torsion. Here is a still finer glass thread, stretched horizontally between two supports: and in order to show its position I have put little jockeys of paper on it. One end is cemented firmly to a wooden block, and the other end is attached to a little instrument called a counter—a little machine for registering the number of revolutions. I now turn this handle till the fibre breaks, and the counter will tell me how many twists I have given this fibre of glass. You see it breaks at twenty revolutions. This is rather a thicker fibre than usual. I have had them bear more than 200 turns without breaking, and some that I have worked with are so fine that if I hold one of them by the end it curls itself up and floats about the room like a piece of spider's thread.

Having now illustrated these properties of glass fibres, I will try to show a very delicate experiment. I want to ascertain the amount of pressure which radiation exerts on a blackened surface. I will put a ray of light on the pan of a balance, and give you its weight in grains; for I think in this Institution and before this audience I may be allowed a scientific use of the imagination, and may speak of weighing that which is not affected by gravitation.

The principle of the instrument is that of W. Ritchie's torsion balance, described by him in the 'Philosophical Transactions' for 1830. The construction is somewhat complicated, but it can be made out on reference to the diagram (Fig. 11). A light beam, A B, having 2 square inches of pith, C, at one end, is balanced on a very fine fibre of glass, D D', stretched horizontally in a tube; one end of the fibre being connected with a torsion handle, E, passing through the tube, and indicating angular movements on a graduated circle. The beam is cemented to the torsion fibre, and the whole is enclosed in glass and connected with the mercury pump by a spiral tube, F, and exhausted as perfectly as possible. G is a spiral spring, to keep the fibre in a uniform state of tension. H is a piece of cocoon silk. I is a glass stopper, which is ground into the tube as perfectly as possible, and then highly polished and lubricated with melted indiarubber, which is the only substance I know that allows perfect lubrication and will still hold a vacuum. The pith, C, represents the scale-pan of the balance. The cross-beam, A B, which carries it, is cemented firmly to the thin glass fibre, D, and in the centre is a piece of mirror, K. Now the cross-beam A B and the fibre D being rigidly connected together, any twist which I give to the torsion handle E will throw the beam out of adjustment. If, on the other hand, I place a weight on the piece of pith C, that end of the beam will fall down, and I shall have to turn the handle, E, round and round a certain number of times, until I have put sufficient torsion on the fibre D to lift up the beam. Now, according to the law of torsion, the force with which a perfectly elastic body like glass tends to untwist itself is directly proportional to the number of degrees through which it has been twisted; therefore, knowing how many degrees of torsion I must put on the fibre to lift up the $\frac{1}{100}$ of a grain weight, I can tell



how many degrees of torsion are required to lift up any other weight; and conversely, putting an unknown weight or pressure on the pith, I can find its equivalent in grains by seeing how much torsion it is equal to. Thus, if $\frac{1}{100}$ of a grain requires 10,000 degrees of torsion, $\frac{1}{80}$ of a grain would require 20,000 degrees; and conversely, a weight which required 5000 degrees torsion would weigh $\frac{1}{200}$ of a grain. Once knowing the torsion equivalent of $\frac{1}{100}$ of a grain, the ratio of the known to the unknown weights is given by the degrees of torsion.

Having thus explained the working of the torsion balance I will proceed to the actual experiment. On the central mirror I throw a ray from the electric light, and the beam reflected on a particular spot of the ceiling will represent zero. The graduated circle J of the instrument also stands at zero, and the counter which I fasten on at the end L stands at O. The position of the spot of light reflected from the little concave mirror being noted, the torsion balance enables me to estimate the pressure or weight of a beam of light to a surprising degree of exactness. I lift up my little iron weight by means of a magnet (for working in a vacuum I am restricted in the means of manipulating), and drop it in the centre of the pith: it knocks the scale-pan down, as if I had placed a pound weight upon an ordinary balance, and the index-ray of light has flown far from the zero-point on the ceiling. I now put torsion on the fibre to bring the beam again into equilibrium. The index-ray is moving slowly back again. At last it is at zero, and on looking at the circle and counter I see that I have had to make 27 complete revolutions and 301 degrees, or $27 \times 360^\circ + 301^\circ = 10,021^\circ$, before the force of torsion would balance the $\frac{1}{100}$ of a grain.

I now remove the weight from the pith-pan of my balance, and liberate the glass thread from torsion by twisting it back again. Now the spot of light on the ceiling is at zero, and the counter and index are again at O.

Having thus obtained the value of the $\frac{1}{100}$ of a grain in torsion degrees, I will get the same for the radiation from a candle. I place a lighted candle exactly 6 inches from the blackened surface, and on removing the screen the pith scale-pan falls down, and the index-ray again flies across the ceiling. I now turn the torsion handle, and in much less time than in the former case the ray is brought back to zero. On looking at the counter I find it registers four revolutions, and the index points to 188 degrees, making altogether $360^\circ \times 4 + 188 = 1628^\circ$, through which the torsion fibre has to be twisted to balance the light of the candle.

It is an easy calculation to convert this into parts of a grain weight; 10,021 torsion degrees representing 0.01 grain, 1628 torsion degrees represent 0.001624 grain.

$$10,021^\circ : 0.01 \text{ grain} :: 1628^\circ : 0.001624 \text{ grain.}$$

The radiation of a candle 6 inches off, therefore, weighs or presses the 2 square inches of blackened pith with a weight of 0.001624 grain.

In my own laboratory, working with this torsion balance, I found that a candle 6 inches off gave a pressure of 0·001772 grain. The difference is only 0·000148 grain, and is fairly within the allowable limits of a discourse experiment. But this balance is capable of weighing to far greater accuracy than that. You have seen that a torsion of 10,021° balanced the hundredth of a grain. If I give the fibre 1 degree more twist the weight is over-balanced, as shown by the movement of the index-ray on the ceiling. Now 1 degree of torsion is about the $\frac{1}{100000}$ part of the whole torsion required by the $\frac{1}{100}$ grain. It represents therefore the $\frac{1}{100000}$ part of the $\frac{1}{100}$, or the millionth part of a grain.

Divide a grain weight into a million parts, place one of them on the pan of the balance, and the beam will be instantly depressed.

Weighed in this balance the mechanical force of a candle 12 inches off was found to be 0·000444 grain; of a candle 6 inches off, 0·001772 grain. At half the distance the weight of radiation should be four times, or 0·001776 grain; the difference between theory and experiment being only four-millionths of a grain is a sufficient proof that the indications of this instrument, like those of the apparatus previously described, follow the law of inverse squares. An examination of the differences between the separate observations and the mean shows that my estimate of the sensitiveness of this balance is not excessive, and that in practice it will safely indicate the millionth of a grain.

I have only had one opportunity of getting an observation of the weight of sunlight: it was taken on December 13th, but the sun was so obscured by thin clouds and haze that it was only equal to 10·2 candles 6 inches off. Calculating from this datum, it is seen that the pressure of sunshine is 2·3 tons per square mile.

But however fair an equivalent ten candles may be for a London sun in December, a midsummer sun in a cloudless sky has a very different value. Authorities differ as to its exact equivalent, but I underestimate it at 1000 candles 12 inches off.

Let us see what pressure this will give:—A candle 12 inches off, acting on 2 square inches of surface, was found equal to 0·000444 grain; the sun, equalling 1000 candles, therefore gives a pressure of 0·444000 grain; that is, equal to about 32 grains per square foot, to 2 cwt. per acre, 57 tons per square mile, or nearly three thousand million tons on the exposed surface of the globe—sufficient to knock the earth out of its orbit if it came upon it suddenly.

It may be said that a force like this must alter our ordinary ideas of gravitation; but it must be remembered that we only know the force of gravity as between bodies such as they actually exist, and we do not know what this force would be if the temperatures of the gravitating masses were to undergo a change. If the sun is gradually cooling, possibly its attractive force is increasing, but the rate will be so slow that it will probably not be detected by our present means of research.

Whilst showing this experiment I wish to have it distinctly under-

stood that I do not attach the least importance to the actual numerical results. I simply wish to show you the marvellous sensitiveness of the apparatus with which I am accustomed to work. I may, indeed, say that I know these rough estimates to be incorrect. It must be remembered that our earth is not a lampblack body enclosed in a glass case, nor is its shape such as to give the maximum of surface with the minimum of weight. The solar forces which perpetually pour on it are not simply absorbed and degraded into radiant heat, but are transformed into the various forms of motion we see around us, and into the countless forms of vegetable, animal, and human activity. The earth, it is true, is poised in vacuous space, but it is surrounded by a cushion of air; and, knowing how strongly a little air stops the movement of repulsion, it is easy to conceive that the sun's radiation through this atmospheric layer may not produce any important amount of repulsion. It is true the upper surface of our atmosphere must present a very cold front, and this might suffer repulsion by the sun; but I have said enough to show how utterly in the dark we are as to the cosmical bearings of this action of radiation, and further speculation would be but waste of time.

It may be of interest to compare these experimental results with a calculation made in 1873, before any knowledge of these facts had been made public.

Professor Clerk Maxwell, in his 'Electricity and Magnetism,' vol. ii. p. 391, writes as follows: "The mean energy in one cubic foot of sunlight is about 0.0000000882 of a foot-pound, and the mean pressure on a square foot is 0.0000000882 of a pound weight. A flat body exposed to sunlight would experience this pressure on its illuminated side only, and would therefore be repelled from the side on which the light falls."

Calculated out, this gives the pressure of sunlight equal to about $2\frac{1}{2}$ lb. per square mile. Between the $2\frac{1}{2}$ lb. deduced from calculation and the 57 tons obtained from experiment the difference is great; but not greater than is often the case between theory and experiment.

In conclusion, I beg to call especial attention to one not unimportant lesson which may be gathered from this discovery. It will be at once seen that the whole springs from the investigation of an anomaly. Such a result is by no means singular. Anomalies may be regarded as the finger-posts along the high road of research, pointing to the bye-ways which lead to further discoveries. As scientific men are well aware, our way of accounting for any given phenomenon is not always perfect. Some point is perhaps taken for granted, some peculiar circumstance is overlooked. Or else our explanation agrees with the facts not perfectly, but merely in an approximate manner, leaving a something still to be accounted for. Now these residual phenomena, these very anomalies, may become the guides to new and important revelations.

In the course of my research anomalies have sprung up in every direction. I have felt like a traveller navigating some mighty river

in an unexplored continent. I have seen to the right and the left other channels opening out, all claiming investigation, and promising rich rewards of discovery for the explorer who shall trace them to their source. Time has not allowed me to undertake the whole of a task so vast and so manifold. I have felt compelled to follow out, as far as lay in my power, my original idea, passing over reluctantly the collateral questions springing up on either hand. To these I must now invite the attention of my fellow-workers in Science. There is ample room for many inquirers.

Nor must we forget that the more rigidly we scrutinize our received theories, our routine explanations and interpretations of nature, and the more frankly we admit their shortcomings, the greater will be our ultimate reward. In the practical world, fortunes have been realized from the careful examination of what has been ignorantly thrown aside as refuse; no less, in the sphere of Science, are reputations to be made by the patient investigation of anomalies.

[W. C.]

Friday, February 18, 1876.

GEORGE BUSK, Esq. F.R.S. Treasurer and Vice-President,
in the Chair.

C. WILLIAM SIEMENS, Esq. D.C.L. F.R.S. M.R.I.

The Action of Light on Selenium.

WHEN, upon former occasions, I have ventured upon this arena, it has been for the purpose of placing before you the results of inquiries of my own into special subjects, which circumstance gave me some title to your indulgence.

This evening I cannot claim the same advantage, because the subject matter which I am about to bring before you is almost entirely the result of the investigations of others, and especially of my brother, Dr. Werner Siemens, who has not the opportunity of addressing you himself.

It is, however, a matter of undoubted interest, and in mentioning some time ago the result of my brother's investigations to my friend Dr. Tyndall, I did so in the hope that he might feel disposed to deal with this subject in his own masterly fashion, and that I should thus procure for the members of the Royal Institution an evening both pleasant and instructive. I did not succeed, however, in obtaining for them such a treat, and it has become my duty to grapple personally with this subject, for which I possess no other qualification than a somewhat intimate acquaintance with a *kindred* subject, that of the influence of heat upon metallic conductors, on which I had the honour of addressing you a few years ago.

Amongst the powers of nature, light seems to be the one which enters least into the composition of matter. The beam of light falling upon the landscape, or upon a work of art, reveals instantly its form to our minds, but with the disappearance of the light its effects seem to vanish entirely: the landscape and the work of art still remain the same, and may be brought back again to our ocular perception, accompanied by all the beautifying effects of light and shade and colour, and yet there seems to be no permanent effect produced in the material condition of the objects before us. Shall we wonder, then, that the true nature of light has remained a mystery more profound than that of the other forces in nature, and that Newton himself exclaimed, in desponding mood, the memorable words, "*Nil luce obscurius.*"

How well does this modest exclamation sit upon the brow of

him who has done more to explain the mysteries of light than all other philosophers both before and after his time ; and how strangely does it contrast with the self-assurance of his antagonists and critics, amongst whom I cannot refrain from citing Goothe, who, himself a moral philosopher, poet, and reader of the human soul of prodigious power, had taken up a branch of science as a pastime, and was evidently prouder of his misconceptions regarding the nature of light than he was of his 'Faust' or 'Wilhelm Meister.' In his 'Farbenlehre' occurs the following allusion to Newton's exclamation before quoted :

" Es sprach ein grosser Physicus
Mit seinen Schulverwandten,
' Nil luce obscurius !'
Ja wohl für Obscuranten."

While Newton laid down incontrovertible principles regarding the nature of light, it has been reserved for physicists of recent times to prove the effects of light upon solids. One of the most beautiful illustrations of the permanent effects of light upon matter is furnished us through photography ; here the ray of light causes the decomposition of compounds of silver in a degree beautifully varying with its intensity.

Another effect of light upon solids is rendered visible by phosphorescent salts, which when acted upon by light continue to glow in various colours for a length of time when taken into a dark room, and I am enabled by the kindness of Mr. Warren De la Rue to show a beautiful series of tubes illustrating this effect.

If anyone required proof that light was a moving force, I would refer him to the discourse delivered in this very place a week ago, when Mr. Crookes gave motion to his radiometer by means of rays of light. But I would go a step farther, and say that light is perhaps the most potential force in nature, because it covers the earth with trees and vegetation of all kinds. It is true that the mushroom thrives in what appears to us utter darkness ; and within the last few days Dr. Higgs has called my attention to a fungus which grows in the deep recesses of the Derbyshire caves, where it lives without the help of light ; but an analysis of this fungus shows that it contains no woody fibre or solid carbon, and so helps to favour the hypothesis *that it is not heat but the ray of light which breaks up carbonic acid in the leaves of plants* in order to separate the carbon. Carbonic acid can indeed be broken up by heat ; but it has been shown by Bunsen and De Ville that a temperature of 2500° C. is necessary for its accomplishment—a degree of heat which would at once destroy all vegetable organization.

Different from these effects of light upon solids is that which forms the subject matter of my discourse, viz. the effect of light upon selenium.

Selenium is an elementary body, which was discovered by Berzelius in 1817 in the residues resulting from the distillation of iron pyrites.

It is fusible, combustible, and similar in many other respects to sulphur, phosphorus, and tellurium. It is in fact one of those substances which are placed by chemists upon the border between metals and metalloids, and, like a true borderer, selenium refuses to be amenable to the laws governing either of these natural groups. If melted (at 217°) and cooled rapidly, it presents a brown amorphous mass of conchoidal fracture, which like sulphur and phosphorus is a non-conductor of electricity. But if a stick of this amorphous selenium is exposed for some time to the heat of boiling water, a structural change becomes observable: it assumes a crystalline fracture, and when again inserted in the galvanic circuit it is found to be a conductor of electricity. Professor Adams has shown recently that its conductivity is different when the current passes through in one direction or the other, and it may here also be observed that its conductivity in this form is still very slight, so that a powerful battery and a delicate galvanometer are necessary to show the effect. The same observer has also found, that, contrary to what takes place in metallic conductors, the conductivity of this substance increases with the power of the battery employed, a circumstance which makes it inapplicable as a substitute for resistance coils in the Wheatstone bridge arrangement.

On the 12th February, 1873, the Society of Telegraph Engineers received a communication from one of its members (Mr. Willoughby Smith *) to the effect that a stick of crystalline selenium, such as had been used for some time in telegraphy where high electrical resistances were required, offered considerably less resistance to a battery current when exposed to light than when kept in the dark. The statement of this observation, which had first been made by Mr. May, Mr. Willoughby Smith's assistant, stationed at Valentia, was received naturally with some incredulity. Could it be possible that the mere superficial action of light upon a solid substance could so change instantaneously its internal condition as to open among its particles flood-gates for the passage of the electric current, to close again upon the removal of the light? Yet the fact announced by Mr. Willoughby Smith was soon corroborated, first, by the Earl of Rosse, who proved clearly that the action was due solely to light, and afterwards by Lieut. Sale, R.N., whose further researches on this subject are described in the 'Proceedings of the Royal Society,' vol. xxi. p. 283, and in Poggendorff's 'Annalen,' bd. 150, s. 333.

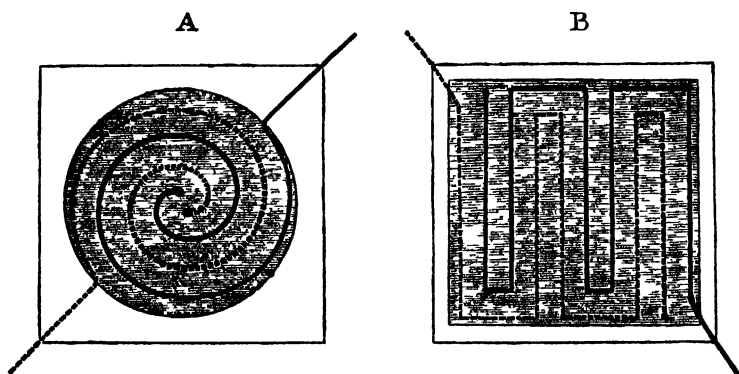
Here the matter rested, when within the last twelve months, it was taken up by two independent inquirers; one in this country and the other in Germany; the one being my friend Professor Adams, of King's College, who has recently communicated the result of his researches to the Royal Society, and the other my brother Dr. Werner Siemens, who has made communications of his results to the Academy of Sciences of Berlin. It is interesting to observe the difference of

* 'Journal of Society of Telegraph Engineers,' vol. ii. p. 31.

methods by which each of these two inquirers arrived at results agreeing on many points of fact, while they differ in the deductions drawn from them, and in their application upon other branches of inquiry. I may here mention that when I expressed my willingness to bring this subject before the Royal Institution, I was not aware that Professor Adams was engaged upon it, and under these circumstances I may be excused if I dwell principally upon my brother's experimental researches, with which I am best acquainted, and regarding which he desires me to acknowledge the valuable assistance rendered him by Dr. Obach.

One of my brother's achievements in his recent researches consisted in giving to the selenium under observation such a form that the surface action produced by the light attains its maximum effect, and that instead of large galvanic batteries and delicate galvanometers being required to obtain indications, one single Daniell cell and a galvanometer of ordinary construction suffice to produce decided results. His sensitive element is composed in the following manner: Two spirals of thin iron or platinum wire are laid upon a small plate of mica in such a manner that the two wires run parallel without touching each other. While in this position a drop of fluid selenium is made to fall upon the plate, filling the interstices between the wires, and before the selenium has had time to harden, another thin plate of mica is pressed down upon it so as to give firmness to the whole. Instead of spirals of wire, a double grating of wire so arranged that the zigzags of the one wire do not touch the interlacing zigzags of the other is sometimes used, and it will be observed that the size of the whole spirals or gratings hardly exceeds the size of a threepenny picce. These are shown in Diagram No. 1.

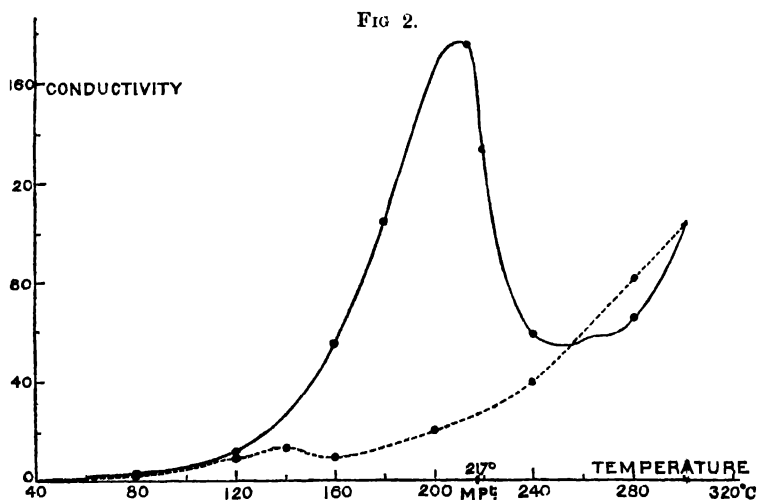
FIG 1



The two protruding ends of the two spirals or gratings serve to insert this selenium element in a galvanic circuit. I here hold an element so prepared of amorphous selenium, which I place in a dark box, and insert in a galvanic circuit comprising a Daniell's cell and

a delicate galvanometer, the face of which will be thrown upon the screen through a mirror by means of the electric lamp. In closing the circuit it will be seen that no deflection of the needle ensues. We will now admit light upon the selenium disc, and close the circuit, when again no deflection will be observed, showing that the selenium in its present condition is a non-conductor both in the dark and under the influence of light. I will now submit a similar disc of selenium, which has been kept in boiling water for an hour and gradually cooled, to the same tests as before. In closing the circuit while the plate is in the dark, a certain deflection of the galvanometer will be discernible, but I will now open the lid of the box so as to admit light upon the disc, when on again closing the circuit a slight deflection of the galvanometer needle will be observed. In closing the box against the light, this deflection will subside, but will again be visible the moment the light is readmitted to the box. Here we have then the extraordinary effect of light upon selenium clearly illustrated.

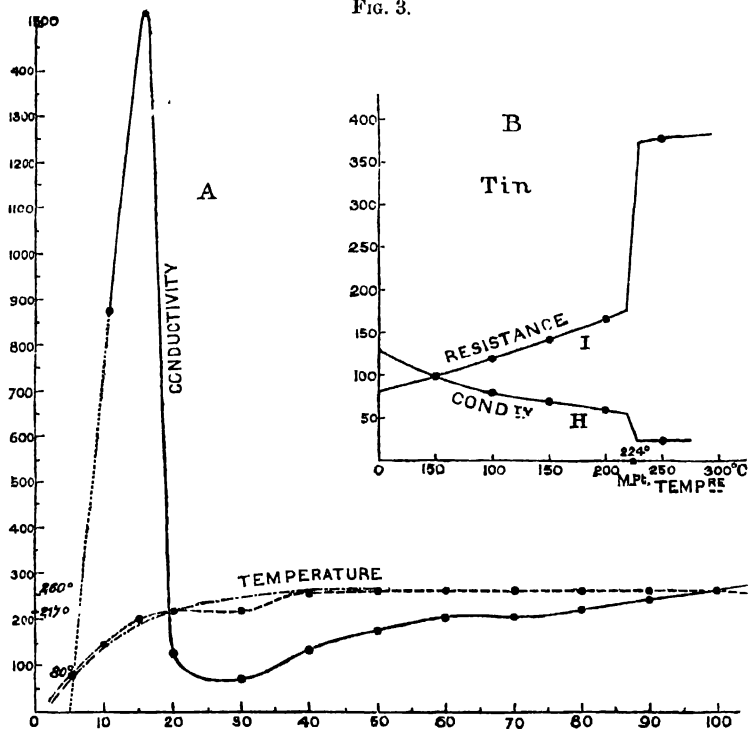
I will now insert into the same circuit another selenium plate which has been heated up to 210°C ., and after having been kept at that temperature for several hours has been gradually cooled; it will be observed that this plate is affected to a greater extent than the former by the action of light, and other conditions to which I shall presently allude prove the selenium heated to a higher temperature to be in other respects dissimilar to the other two modifications of the same.



These differences will be best revealed in describing my brother's experiment. He placed one of his amorphous preparations of selenium in an air bath heated above the melting point of selenium (to 260°C .), while the connecting wires were inserted in a galvanic circuit con-

sisting of only one Daniell's element and a delicate reflecting galvanometer, and every five minutes the temperature and conductivity of the selenium were noted. The results obtained are shown on the Diagram No. 2, in which the abscissæ represent temperatures, and the ordinates the conductivity of the selenium while in the dark. It will be observed that up to the temperature of 80° C. no current passed, that from this point onward the conductivity of the material rapidly increased until it attained its maximum at the temperature of 210° C., being nearly its melting point, after which an equally rapid diminution of conductivity commenced, reaching a minimum at the temperature of about 240° C., when the conductivity was only such as could be detected by a most delicate galvanometer. In continuing to increase the temperature of the fluid selenium very gradually but steadily, its conductivity increased again. The dotted line shows the conductivity on cooling.

FIG. 3.



The curves on Diagram No. 3 give a comparison between the effects which actually take place in heating the selenium, and what would take place if the selenium did not melt nor undergo chemical change during heating. In this case the abscissæ represent

periods in minutes from the commencement of the plunging of the selenium into the hot bath, while the ordinates represent conductivity and temperature respectively, on the curves, as marked. Up to the temperature of 88°C ., the actual and theoretical curve accord exactly, but from this point onward the temperature of the selenium took the lead of that shown on the theoretical curve, firstly proving a spontaneous liberation of heat within the mass, and secondly an absorption of heat during melting, as indicated by the relative positions of the curves at the melting point 217°C . The beginning and end of the two curves correspond exactly. The theoretical curve is marked —.—.—.

The interpretation of these experiments, which are of too delicate and elaborate a nature to be repeated here, is as follows: Amorphous selenium retains a very large amount of specific heat, which renders it a non-conductor of electricity: when heated to 80° , this amorphous solid mass begins to change its amorphous condition for the crystalline form, in which form it possesses a greatly reduced amount of specific heat, giving rise to the increase of temperature beyond that of surrounding objects when the change of condition has once set in. If care is taken to limit the rise of temperature of the selenium to 100°C ., and if it is very gradually cooled after having been maintained for an hour or two at that temperature, a mass is obtained which conducts electricity to some extent, and which shows increased conductivity under the influence of light. But in examining the conductivity of selenium so prepared at various temperatures below 80° , and without accession of light, it was found that its *conductivity increases with rise of temperature*, in which respect it resembles carbon, sulphide of metals, and generally the electrolytes. This my brother terms his first modification of selenium. But in extending the heating influence up to 210° , and in maintaining that temperature by means of a bath of paraffin for some hours before gradually reducing the same, he obtained a second modification of selenium in which its conductivity increases with fall of temperature, and in which modification it is therefore analogous to the metals. This second modification of selenium is a better conductor of electricity than the first, and its sensitiveness to light is so great that its conductivity in sunlight is fifteen times greater than it is in the dark, as will be seen from the following table, and in Diagram No. 4, in which is given the effects of different intensities of light on selenium (Modification II.) obtained at Woolwich on the 14th February, 1876:

Selenium in	Relative Conductivities.		Resistance in Ohms.
	Deflections	Ratio.	
1. Dark	32	1	10,070,000
2. Diffused daylight	110	3.4	2,930,000
3. Lamplight	180	5.6	1,790,000
4. Sunlight	470	14.7	680,000

It is not, however, so much in relation to other elements that vanadium is interesting, as by virtue of the remarkable properties which the metal itself possesses. Thus the lowest stage of oxidation which the element can assume, viz. V_2O_2 , is a powerful reducing agent, bleaching indigo by reduction almost as quickly as chlorine does by oxidation. On allowing the solution thus bleached to stand, the hypovanadous salt at once takes up oxygen from the air, and indigo blue appears again. On the other hand, the highest oxide V_2O_5 parts with its oxygen readily, and is easily reduced by organic matter to a lower oxide; acting in this respect like the highest oxide of chromium CrO_3 .

This property of vanadic acid enables this substance to be employed in photography.* If gelatine be mixed with sodium divanadate, and the film unexposed to light, the portions strongly insolated become slightly less soluble in warm water than the non-exposed portion, so that it is possible to print from such a film. Again, if paper which does not contain any animal size is coated with a solution of sodium ortho-vanadate and then exposed to light, the portion insolated assumes a dark tint dependent upon the length of exposure and the strength of the solution employed. If the paper thus prepared be immersed, after exposure, in a solution of silver nitrate, the colour in the exposed part instantly changes to a dark brown or black colour, doubtless due to the reduction of the silver salt by the vanadous compound formed in the paper. Paper thus prepared may be used for photographic printing. The unexposed portions of the print are in this process coated with yellow silver ortho-vanadate; but this can be completely removed by ammonia or by sodium hyposulphite. Silver ortho-vanadate is capable of forming a latent image, like the chloride or bromide, and this may be developed by the ordinary ferrous developer. Two or three minutes' exposure to sunlight is needed. In the development little or no silver nitrate must be present.

By far the most important and interesting application of vanadium is, however, that recently suggested for the preparation of a permanent black which is now largely coming into use amongst dyers and calico printers, and is already extensively employed as a permanent marking ink.

Of the commercial value of a permanent rich black dye it is difficult for the uninitiated in such matters to form an idea. Suffice it to say that it is very great. We must, however, remember that this application of vanadium is only in its infancy, and whether the vanadium black will realize all the requirements of practice is a question which can only be settled by long and patient inquiry; still it has already so far proved a success that we may look forward with confidence to its future.

It is not at first sight easy to understand how a rare substance like

This proposal was first made by Mr. James Gibbons in 1874.

vanadium, the price of which not long ago was 1s. 6d. per grain, and which even now cannot be obtained for less than $\frac{1}{2}$ d. a grain, can be employed for the production of a black colour, which, if not cheap and able to compete with the other common dyes, is of course useless in a practical and commercial point of view.

In order to understand the possibility of the technical application of one of Nature's rarest gifts, the history of the preparation of aniline black must be noticed. The splendid red, crimson, violet, green, and blue colours which are obtained from aniline are now universally known and appreciated, and their wide-spread manufacture serves as a striking illustration of the value of original scientific investigation. It is, however, not so generally known that not only the bright and gay colours, but also sombre browns and jetty blacks—by far the most valuable because by far the most generally used of colours—can be obtained from aniline.

In the year 1860, Mr. John Lightfoot, calico printer, of Accrington, applied to the processes of calico printing a black colouring matter which had been previously obtained in the manufacture of mauve from aniline by Messrs. Roberts, Dalo and Co., of Manchester.

This black colouring matter is invariably formed when either aniline or toluidine, or mixtures of these two substances, are subjected to oxidizing actions; but in spite of several researches which have recently been published on aniline black, we are as yet unacquainted with its chemical formula, nor indeed can we say that it even possesses a constant chemical composition.

In order that a colouring matter shall be fixed or permanent, it must be fastened in some way to the fibre of the cloth. In the case of cotton this is generally effected (1) either by the precipitation of the soluble colouring matter in the fibre by means of a mordant which forms an insoluble compound termed a lake with the colour, as in madder dyeing and steam-colour printing; or (2) by the fixation of the colour by means of albumen, as in pigment printing; or (3) by the gradual oxidation and consequent precipitation of the colouring matter in the fibre, as in indigo printing. It is to this latter class of processes that aniline-black dyeing or printing belongs; for the aniline salt under the action of certain oxidizing agents passes more or less quickly from the condition of a colourless solid readily soluble in water, into that of a black amorphous insoluble powder not to be distinguished at first sight from soot. Hence if the cloth can be impregnated with the aniline and with the oxidizing agent at the same time, and if the process of oxidation can be allowed to go on in the fibre, the black will be formed and will be permanently fixed in the fabric.

Many oxidizing agents, such as chlorine, ozone, or electrolytic oxygen, have the power of transforming aniline into this black pigment. In most cases a high temperature is needed for this purpose. Thus, for instance, if aniline is heated with chlorate of sodium, and if then hydrochloric acid be carefully added, a deep black

almost solid mass is produced. In order, however, that the process may be employed in dyeing and calico printing, it is absolutely necessary to avoid high temperatures as well as the action of strong acids, because when exposed to these the cloth invariably is rotted or becomes "tender." If a mere mixture of aniline salt and chlorate of potash be heated strongly enough, the black is formed; but the heat necessary to produce the colour is sufficient, together with the hydrochloric acid which is at the same time liberated by the decomposition, to make the cloth rotten, and therefore to render this process useless.

It was found by Lightfoot that if an addition of 4 ounces of nitrate of copper solution was made to the pound of aniline and to the chlorate, the oxidation of the aniline went on at a lower temperature than when the copper salt was absent, and hence, when carefully worked, the black could be formed by this process without tendering the cloth. Certain technical objections to this process, however, soon arose; and in 1865 Lauth proposed to use the insoluble copper sulphide instead of the soluble nitrate, by which means he prevented the deposition of copper on the "rollers" and on the "doctors" which took place in Lightfoot's process. The method thus modified has been and is now extensively used for the production of black, and the chief, if not the only, objection which can be urged against it is that the black thus obtained is not perfectly permanent, but is liable to become green when exposed to reducing agents, such as the sulphurous acid contained in the impure air of our towns. This is, however, a serious drawback, and one which those practically engaged in solving such problems have not been able to remove. So much so indeed is this the case, that it is generally believed that the property of aniline black to become green when exposed to sulphurous acid, and to return to the black when treated with alkalis, is an essential property of the substance, which may be compared with the property of litmus to change colour in presence of acids and alkalis.

That the aniline black can not only be produced in presence of copper but also, as Mr. Lightfoot showed in the year 1871, in presence of vanadium salts, and that by vanadium alone can the black be obtained of the requisite permanent character, has now been proved beyond doubt. Moreover, the quantity of the vanadium necessary in order to produce the oxidation of the aniline is about one thousand times less than that of the copper. Thus if a piece of calico be dipped into a solution of 2.5 grains of vanadate of ammonia dissolved in a gallon of water and then dried, the cloth thus prepared is capable of producing an intense black if treated with the mixture of aniline salt and chlorate. In the same way if 1 gallon of colour be made containing 20 ounces of aniline hydrochlorate, 10 ounces of chlorate of soda, and 3 grains of vanadate of ammonia, a mixture is obtained with which no less than from 20 to 25 pieces, or from 500 to 600 yards of cloth, such as that exhibited, can be thus printed of a permanent black.

In dyeing also, the vanadium will be extensively used ; and in the same way only mere traces of this rare metal are requisite, whereas the copper black cannot be used for dyeing. Thus, for instance, 1 gallon of colour intense enough to dye 40 lbs. of cotton yarn black is obtained by mixing 8 ounces of aniline hydrochlorate, 4 ounces of sodium chlorate, and 8 grains of vanadate of ammonia. Cotton, wool, or silk dipped twice into this mixture and then aged, or allowed to oxidize, and "raised" in a solution of carbonate of soda, is dyed a deep rich and permanent blue black. The goods may also be allowed to steep in a bath of the above strength for three days, then well washed in warm water, or boiled in a weak solution of acetic acid, to remove any bronzo colour found on the surface of the silk or wool. The permanent black is then formed, and the fibre found to be quite strong.

The part played by vanadium in the formation of the black colour may be easily explained, when we remember the ease with which the metal passes from one degree of oxidation to another, thus from V_2O_5 , the highest degree, to V_2O_4 , and *vice versa*. In this way it doubtless acts, as M. Guyard has suggested, as a carrier of the oxygen of the chlorate to the aniline, being alternately reduced and re-oxidized, so that an infinitely small quantity of vanadium compound will convert an infinitely large quantity of aniline salt into anilino black, reminding one of the action of nitrous fumes in the leaden chamber.

Some time after the discovery of aniline black, Mr. Robert Pinkney, of the firm of Messrs. Blackwood and Co., of London, discovered, independently of Mr. Lightfoot, that vanadium can be most advantageously substituted for copper in the formation of aniline black ; and he employed this reaction for the preparation of a permanent marking ink termed "Jetoline," of which many thousands of bottles have been sold. A few grains of vanadium—say from seven to twelve—being sufficient to produce, together with hydrochlorate of aniline and chlorate of soda, a gallon of marking ink.

The subject of the use of vanadium as a valuable dyeing agent was next taken up by the Magnesium Metal Company, of Patricroft, near Manchester ; and, thanks to the unwearied exertions of Mr. Samuel Mellor, this firm have now succeeded not only in securing a very considerable supply of the rare element which occurs in the Keuper sandstone as the new mineral Mottramite, but are now in a position to produce a vanadium black for both calico printing and dyeing which is perfectly permanent. This is the more remarkable, as up to this time no aniline black made with copper has been produced in commerce which will withstand the reducing action of sulphurous acid.

As the result of a large number of experiments made with various qualities of commercial aniline, and by varying the strengths of solutions, proportions of aniline and sodium chlorate employed, and also by altering the temperature and the conditions of ageing, Mr. Mellor

has found (1) that within certain limits the purer the aniline used, the deeper and more permanent is the black obtained. (2) That there is a maximum density of colour, beyond which if larger proportions of aniline salt and chlorate are used, corresponding advantages of colour are not obtained. This maximum colour is yielded by 16 ounces to 20 ounces of hydrochlorate of aniline per gallon of colour. (3) That for the formation of a permanent black, the amount of aniline salt and sodium chlorate used for 1 gallon of colour must bear a definite relation to each other, the weight of sodium chlorate being about one-half that of the aniline hydrochlorate used. (4) That the permanency of the black depends very much upon the care and skill shown in "ageing" the cloth. If the cloth is aged in a moist atmosphere a blue-black is developed, which is very fleeting; but if aged in a dry air, and at a high temperature, a permanent black is obtained. It is also interesting to learn that for other colours also, the use of vanadium appears to be of value, as in the production of catechu browns as well as in some of the brighter aniline dyes.

It is indeed impossible to say what important technical functions this rare and hitherto unapplied substance may not fulfil. Only the other day vanadium was accounted one of our greatest chemical curiosities, and the investigation of its properties would have been thought, by the practical Englishman, to be a mere waste of time.

Now, however, we have in vanadium a new example of the value of pure scientific research, which must carry conviction even to the most utilitarian of minds.

[H. E. R.]

Friday, February 2, 1877.

SIR T. FREDERICK ELLIOT, K.C.M.G. Vice-President, in the Chair.

PROFESSOR OSBORNE REYNOLDS,

OWENS COLLEGE, MANCHESTER

Vortex Motion.

IN commencing this discourse the author said, Whatever interest or significance the facts I hope to set before you may have, is in no small degree owing to their having, as it were, eluded the close mathematical search which has been made for them, and to their having in the end been discovered in a simple, not to say commonplace, manner. In this room you are accustomed to have set before you the latest triumphs of mind over matter, the secrets last wrested from nature by gigantic efforts of reason, imagination, and the most skilful manipulation. To-night, however, after you have seen what I shall endeavour to show you, I think you will readily admit that for once the case is reversed, and that the triumph rests with nature, in having for so long concealed what has been so eagerly sought, and what is at last found to have been so thinly covered.

The various motions which may be caused in a homogeneous fluid like water, present one of the most tempting fields for mathematical research. For not only are the conditions of the simplest, but the student or philosopher has on all hands the object of his research, which, whether in the form of the Atlantic waves or of the eddies in his teacup, constantly claims his attention. And, besides this, the exigencies of our existence render a knowledge of these motions of the greatest value to us in overcoming the limitations to which our actions are otherwise subject.

Accordingly we find that the study of fluid motion formed one of the very earliest branches of philosophy, and has ever since held its place, no subject having occupied the attention of mathematicians more closely. The results have been, in one sense, very successful; most important methods of reasoning have been developed, mathematical methods, which have helped to reveal numberless truths in other departments of science, and have taught us many things about fluids which most certainly we should not otherwise have found out, and of which we may some day find the application. But as regards the

direct object in view, the revelation of the actual motion of fluids, the research has completely failed. And now that generations of mathematicians have passed away, now that the mysteries of the motions of the heavenly bodies, of the earth itself, and almost of every piece of solid matter on the earth have been explained by mathematicians, the simplest problems of fluid motion are yet unsolved.

If we draw a disc flatwise through the water, we know by a process of unconscious geometrical reasoning that the water must move round the disc; but by no known mathematical process could the motion be ascertained from the laws of motion. If we draw the plate obliquely through the water we experience a greater pressure on the one side than on the other. Now this case, representing as it does the principle of action of the screw propeller, is of the very highest importance to us; and yet, great as has been the research, it has revealed no law by which we may in a given case calculate the resistance to be obtained, or indeed tell from elementary principles in what way the water moves to let the plate pass. Again, the determination of the resistance which solid bodies, such as ships, encounter is of such exceeding economic importance, that theory, as shipbuilders call it, having failed to inform them what to expect, efforts have been, and are still being, made to ascertain the laws by direct experiment. Instances might be multiplied, but one other must suffice. If we send a puff of fluid into other fluid we know that it will travel to a considerable distance, but the manner in which it will travel and the motion it will cause in the surrounding fluid, mathematics have not revealed to us.

Now the reasons why mathematicians have thus been baffled by the internal motions of fluids appear to be very simple. Of the internal motions of water or air we can see nothing. On drawing the disc through the water there is no evidence of the water being in motion at all, so that those who have tried to explain these results have had no clue; they have had not only to determine the degree and direction of the motion, but also its character.

But although the want of a clue to the character of the motion may explain why so little has been done, it is not so easy to understand how it is that no attempts were made to obtain such a clue. It would seem that a certain pride in mathematics has prevented those engaged in these investigations from availing themselves of methods which might reflect on the infallibility of reason.

Suggestions as to the means have been plentiful. In other cases where it has been necessary to trace a particular portion of matter in its wanderings amongst other exactly similar portions, ways have been found to do it. It may be argued that the influences which determine the path of a particular portion of water are slight, subtle, and uncertain, but not so much so as those which determine the path of a sheep. And yet thousands of sheep have been from time immemorial turned loose on the mountains belonging to different owners, and although it probably never occurred to anyone to reason out the paths

of his particular sheep, they have been easily identified by the aid of a little colour. And that the same plan might be pursued with fluids, every column of smoke has been evidence.

But these hints appear to have been entirely neglected, and it was left for nature herself, when, as it were, fully satisfied with having maintained her secret so long, and tired of throwing out hints which were not taken, at last to divulge the secret completely in the beautiful phenomenon of the smoke ring. At last; for the smoke ring is probably a phenomenon of modern times. The curls of smoke, as they ascend in an open space, present to the eye a hopeless entanglement; and although, when we know what to look for, we can see as it were imperfect rings in almost every smoke cloud, it is rarely that anything sufficiently definite is formed to attract attention, or suggest anything more important than an accidental curl. The accidental rings, when they are formed in a systematic manner, come either from the mouth of a gun, the puff of a steam engine, or the mouth of a smoker, none of which circumstances existed in ancient times.

Although, however, mathematicians can in no sense be said to have discovered the smoke ring, or the form of motion which it reveals, they were undoubtedly the first to invest it with importance. Had not Professor Helmholtz some twenty years ago called attention to the smoke ring by the beautiful mathematical explanation which he gave of its motion, it would in all probability still be regarded as a casual phenomenon, chiefly interesting from its beauty and rarity. Following close on Helmholtz came Sir William Thomson, who invested these rings with a transcendental interest by his suggestions that they are the type after which the molecules of solid matter are constituted.

The next thing to enhance the interest which these rings excited, was Professor Tait's simple and perfect process of producing them at will, and thus rendering them subjects for lecture-room experiments. Considering that this method will probably play a great part in perfecting our notions of fluid motion, it is an interesting question how Professor Tait came to hit upon it. There is only one of the accidental sources of these rings which bears even a faint resemblance to this box, and that is the mouth of a smoker as he produces these rings. This might have suggested the box to Professor Tait. But since this supposition involves the assumption that Professor Tait sometimes indulges in a bad habit, and as we all know that Professor Tait is an eminent mathematician, perhaps we ought rather to suppose that he was led to his discovery by some occult process of reasoning which his modesty has hitherto kept him from propounding.

But however this may be, his discovery was a most important one, and by its means the study of the actual motion of these rings has been carried far beyond what would otherwise have been possible.

But it has been for their own sake, and for such light as they might throw on the constitution of matter, that these rings were studied.

The most important lesson which they were capable of teaching still remained unlearned. It does not appear to have occurred to anyone that they were evidence of a general form of fluid motion, or that the means by which these had been revealed, would reveal other forms of motion.

There was, however, at least one exception, which will not be forgotten in this room: the use of smoke to show the effect of sound upon jets of air.

Also, the late Mr. Henry Deacon, in 1871, showed that minute vortex rings might be produced in water by projecting a drop of coloured water from a small tube. And his experiments, in spite of their small scale, excited considerable interest.

Four years ago, being engaged in investigating the action of the screw propeller, and being very much struck by the difference between some of the results he obtained and what he had been led to expect, the author made use of colour to try and explain the anomalies when he found that the vortex played a part in fluid motion which he had never dreamt of; that, in fact, it was the key to almost all the problems of internal fluid motion. That these results were equally new to those who had considered the subject much more deeply than he had, did not occur to him until after some conversation with Mr. Froude and Sir William Thomson.

Having noticed that the action of the screw propeller was greatly affected when air was allowed to descend to the blades, he was trying what influence air would have on the action of a simple oblique vane, when a very singular phenomenon presented itself. The air, instead of rising in bubbles to the surface, ranged itself in two long horizontal columns behind the vane. There was evidence of rotational motion about these air lines. It was evident, in fact, that they were the central lines of two systematic eddies.

That there should be eddies was not surprising, but eddies had always been looked upon as a necessary evil which besets fluid motion as sources of disturbance, whereas here they appeared to be the very means of systematic motion.

Here then was the explanation of the nature of the motion caused by the oblique vane, a cylindrical band of vortices continually produced at the front of the plate, and falling away behind it in an oblique direction.

The recognition of the vortex action caused behind the oblique vane, suggested that there might be similar vortices behind a disc moving flatwise through the water, such as are the eddies caused by a teaspoon.

There was one consideration, however, which at first seemed to render this improbable. It was obvious that the resistance of the oblique vane was caused in producing the vortices at its forward part; so that if a vortex were formed behind a flat plate, as this vortex would remain permanently behind, and not have to be continually elongated, the resistance should diminish after the plate was once set in motion;

whereas experience appeared to show that this was by no means the case. It appeared probable, therefore, that from some disturbing cause the vortex would not form, or would only form imperfectly, behind the plate.

This view was strengthened when, on trying the resistance of a flat plate, it did not appear to diminish after the plate had been started.

Accidentally, however, it was found that if the float to which the plate was attached was started suddenly and then released, the float and plate would move on apparently without any resistance. And more than this, for if the float were suddenly arrested and released, it would take up its motion again, showing that it was the water behind that was carrying it on.

There was evidence therefore of a vortex behind the disc. In the hope of rendering this motion visible, coloured water was injected in the neighbourhood of the disc, and then a beautiful vortex ring, exactly resembling the smoke ring, was seen to form behind the disc. If the float were released in time, this ring would carry the disc on with it; but if the speed of the disc were maintained uniform, the ring gradually dropped behind and broke up. Here then was another part played by the vortex previously undreamt of.

That the vortex takes a systematic part in almost every form of fluid motion was now evident. Any irregular solid moving through the water must from its angles send off lines of vortices such as those behind the oblique vane. As we move about we must be continually causing vortex rings and vortex bands in the air. Most of these will probably be irregular, and resemble more the curls in a smoke cloud than systematic rings. But from our mouths as we talk we must produce numberless rings.

One way in which rings are produced in perhaps as great numbers as from our mouths is by drops falling into the sea. If we colour the surface of a glass vessel full of water, and then let drops fall into it, rings are produced, which descend sometimes as much as two or three feet.

But the most striking rings are those produced in water, in a manner similar to that in which the smoke rings are produced, using coloured water instead of smoky air.

These rings are much more definite than smoke rings, and although they cannot move with higher velocities, since that of the smoke ring is unlimited, the speed at which they move is much more surprising.

In the air we are accustomed to see objects in rapid motion, and so far as our own notions are concerned, we are unaware of any resistance; but this is quite otherwise in water. Every swimmer knows what resistance water offers to his motions, so that when we see these rings flash through the water we cannot but be surprised. Yet a still more striking spectacle may be shown, if, instead of coloured water, a few bubbles of air be injected into the box from which the puff is sent; a beautiful ring of air is seen to shoot along through the water,

showing, like the lines of air behind the oblique vane, little or no tendency to rise to the surface.

Such is the ease with which these vortex rings in water move, and so slight is the disturbance which they cause in the water behind them, as to lead to the conclusion that they experience no resistance whatever, except perhaps a little caused by slight irregularities in their construction. Their velocity gradually diminishes; but this would appear to be accounted for by their growth in size, for they are thus continually taking up fresh water into their constitution, with which they have to share their velocity. Careful experiments have confirmed this view. It is found that the force of the blow they will strike is nearly independent of the distance of the object struck from the orifice.

The discovery of the ring behind the disc afforded the opportunity of observing the characteristics of these rings much better than was afforded by the smoke rings; and also suggested facts which had previously been overlooked. The manner of motion of the water which formed the ring and of the surrounding water was very clearly seen. It was at once seen that the visible ring, whether of coloured water or air, was merely the central line of the vortex; that it was surrounded by a mass of coloured water, bearing something the same proportion to the visible ring as a ball made by wrapping string (in and out) round a curtain ring until the aperture was entirely filled up. The disc, when it was there, formed the front of this ball or spheroid of water, but the rest of the surface of the ball had nothing to separate it from the surrounding water but its own integrity. Yet when the motion was very steady the surface of the ball was definite, and the entire moving mass might be rendered visible by colour. The water within the ball was everywhere gyrating round the central ring, as if the coils of string were each spinning round the curtain ring as an axis, the water moving forwards through the interior of the ring and backwards round the outside, the velocity of gyration gradually diminishing as the distance from the central ring is increased.

The way in which the water moves to let the ball pass can also be seen, either by streaking the water with colour or suspending small balls in it. In moving to get out of the way and let the ball of water pass, the surrounding water partakes as it were of the gyrating motion of the water within the *ball*, the particles moving in a horse-shoe fashion, so that at the actual surface of the *ball* the motion of the water outside is identical with that within, and there was no rubbing at the surface, and consequently no friction.

The maintenance of the shape of the moving mass of water against the unequal pressure of the surrounding water as it is pushed out of the way is what renders the internal gyratory motion essential to a mass of fluid moving through a fluid. The centrifugal force of this gyratory motion is what balances the excess of pressure of the surrounding water in the front and rear of the ball, compared with what it is at the sides.

It is impossible to have a ring in which the gyratory motion is great, and the velocity of progression slow. As the one motion dies out so does the other, and any attempt to accelerate the velocity of the ring by urging forward the disc, invariably destroyed it.

The striking ease with which the vortex ring, or the disc with the vortex ring behind it, moves through the water, naturally raised the question as to why a solid should experience resistance. Could it be that there was something in the particular spheroidal shape of these balls of water which allowed them to move freely. To try this, a solid of the same shape as the fluid ball was constructed and floated after the same manner as the disc. But when this was set in motion, it stopped directly—it would not move at all. What was the cause of this resistance? Here were two objects of the same shape and weight, the one of which moved freely through the water, and the other experienced very great resistance. The only difference was in the nature of the surface. As already explained, there is no friction at the surface of the water, whereas there must be friction between the water and the solid. But it could be easily shown that the resistance of the solid is much greater than what is accounted for by its surface friction or skin resistance. The only other respect in which these two surfaces differ is that the one is flexible, while the other is rigid, and this seems to be the cause of the difference in resistance.

If ribbons be attached to the edge of the disc, these ribbons will envelope the ball of water which follows it, presenting a surface which may be much greater than that of the solid; and yet this, being a flexible surface, the resistance of the disc with the vortex behind it is not very much greater than it would be without the ribbons—nothing to be compared to that of the solid.

Colouring the water behind the solid shows, that instead of passing through the water without disturbing it, there is very great disturbance in its wake. An interesting question is as to whether this disturbance originates with the motion of the solid, or only after the solid is in motion. This is settled by colouring the water immediately in front of the solid before it is started. Then on starting it the colour is seen to spread out in a film entirely over the surface of the solid, at first without the least disturbance, but this follows almost immediately.

Among the most striking features of the vortex rings, is their apparent elasticity. When disturbed they not only recover their shape, but vibrate about their mean position like an elastic solid. So much so, as to lead Sir William Thomson to the idea that the elasticity of solid matter must be due to its being composed of vortex rings.

But apart from such considerations, this vibration is interesting as showing that the only form of ring which can progress steadily is the circular. Two parallel bands, such as those which follow the oblique vane, could progress if they were infinitely long, but if not, they must be continually destroyed from the ends. Those which

follow the oblique vane are continually dying out at one end, and being formed again at the other.

If an oval ring be formed behind an oval plate, the more sharply curved parts travel faster than the flatter parts; and hence, unless the plate be removed, the ring breaks up. It is possible, however, to withdraw the plate, so as to leave the oval ring, which proceeds wriggling along each portion moving in a direction perpendicular to that in which it is curved, and with a velocity proportional to the sharpness of the curvature. So that not only does the ring continually change its shape, but one part is continually falling behind, and then overtaking the other.

These were some of the forms of fluid motion which imagination or reason had failed to show us, but which had been revealed by the simple process of colouring the water.

Now that we can see what we are about, mathematics can be most usefully applied; and it is expected that when these facts come to be considered by those best able to do so, the theory of fluid motion will be placed on the same footing as the other branches of applied mechanics.

[O. R.]

Friday, February 16, 1877.

SIR T. FREDERICK ELLIOT, K.C. M.G. Vice-President, in the Chair.

PROFESSOR FREDERICK GUTHRIE, F.R.S.

Solid Water.

WHEN, some months ago, I received, through your excellent Secretary, a notification of your wish that I should undertake one of these Friday evening discourses, I looked upon the invitation as a command: as a command, if for no other reason, because, for some years past, I have, through your courtesy, been privileged to participate between these walls in many a rare intellectual treat.

As I cast about for a suitable subject, I felt sure that, at your hands, I should not incur the charge of egoism if I brought before you, as briefly and simply as I could, the results of some experimental researches which for the last few years have engrossed my leisure time. And whatever hesitation I had in selecting a subject of this nature, has been obliterated by the feeling that what I have to speak of to-night illustrates a generalization which, I think, has not hitherto been enunciated with sufficient distinctness, but which may be maintained with great show of reason. I will not call it a law of nature, for they who use the term law in connection with natural phenomena are, I believe, neither sufficiently alive to the insignificance of law, nor to the omnipotence of nature. Let me therefore call what I mean by the more expressive, because more ambiguous, term "Generalization." It is this: "Substances which are most abundant are in their nature most exceptional." At once, among the elements we find that great trinity, oxygen, hydrogen, and nitrogen, standing as a group far removed from other elements, only to differ from one another by immeasurable intervals. The metal sodium, than which there is none more remarkable, is perhaps the most abundant; while the rarer metals, such as gold, platinum, osmium, iridium, &c., have many characteristics in common.

It will not do to push this proposition too far: for even as I spoke, instances have occurred to you, as they have to me, where the generalization appears at least to fail. If, however, I wished to adduce the strongest testimony in its favour, I should speak of water, a compound body, and of all compound bodies as simple as any, and

perhaps as abundant. Let me glance at the properties which render it pre-eminent. Of all compound liquids, it has by far the greatest hardness or cohesion. Gather under like circumstances drops of water and of all other known liquids, and you will find those of water the largest. Endeavour to pass radiant heat through it, and you find it resists such passage with the greatest stubbornness: it is eminently athermanous. But compare its power of allowing heat of contact to pass through, and you find it to be by far the best liquid heat conductor. Examine its capacity for heat, and you find that it here exceeds all known liquids, with one exception, and that exception is a mixture containing a large proportion of water. Cast light on it, and it bends that light less than any substance, excepting its own offspring, ice. Finally, it enjoys that rare and almost unique property of having a state of maximum density at a temperature above its freezing point.

On all these grounds, the expression of the old Greek,

ἀριστον μὲν ὑδωρ,

seems to have been prophetic, if we understand *αριστος* in its simple sense of pre-eminence.

I propose this evening to consider mainly one faculty of water, namely, its power of dissolving that innumerable class of bodies called salts, which may, I suppose, without much danger of a misunderstanding, be considered as bodies soluble in water, and which contain metals. I wish to consider the relationship between the water and the salt it has dissolved, and I desire to direct especial attention to the circumstances under which water becomes solid in presence of and in combination with other bodies.

Water may become solid in a variety of ways. First, by itself, losing heat, it becomes ice ; secondly, when thrown upon quick lime and similar bodies, by the loss of heat it becomes along with the lime a solid, slaked lime ; thirdly, if you pour water upon dried alum and similar bodies, and let the solution stand, you get dry crystals, I dare scarcely say containing water, but from which water can be readily got. Again, if you boil glue or isinglass with water, you get a more or less solid jelly, according to the quantity of water you employ.

These various ways by which water may be solidified result in the more or less complete obliteration of its character as water. Chemists tell us that in the slaking of lime we do not witness the mere juxtaposing of a molecule of water alongside a molecule of lime, but rather a double decomposition whereby the molecules of each constituent are decomposed and one or two new molecules are formed ; *

* Not $\text{CaO} + \text{HO} = \text{CaOHO}$, but $\text{Ca}_2\text{O} + \text{H}_2\text{O} = 2\text{CaHO}$,
 (Ca = 20, H = 1, O = 8) or $\text{CaO} + \text{H}_2\text{O} = \text{Ca}_2\text{HO}$.
 (Ca = 40, H = 1, O = 16)

and that when by heat the water from slaked lime is recovered, recomposition of quick lime and of water ensues. Far less violent is the action when burnt alum dissolves in water, and far more readily are the two again separated: while from the ordinary "washing soda" in moderately dry air the water gradually escapes by diffusion into the air. Yet in all these cases the water is held by the solid with some strength. Lastly, when gluc or gum dissolves in water there appears to be no energy expended in the act of solution, they mix even as two gases mix.

Strictly speaking, when a grain of salt dissolves in a gallon of water both are destroyed; the salt ceases to be salt and the water ceases to be water: the two form a salt solution. This fact must never be forgotten, but its strict observance would land us here in the cumbersome restriction of denying the name of water to the liquids of our springs, rivers, and seas.

On the table you see examples of the various kinds of solid water. And first stands ice. In this room it is unnecessary for me to speak especially of this substance, which has formed for you the basis of so many an eloquent discourse. Again, there is water of combination, of constitution, of gelatinization, and of crystallization.

It is to be remarked, and is indeed for our present purpose most noteworthy, that whole classes of salts are known which solidify with water of crystallization, while others of no noticeable chemical difference reject water as they build themselves together. Nay, more, that salts most closely allied to one another in their chemical nature combine with water of crystallization in very different proportions. What is there peculiar in saltpeter, in lunar caustic, in sal-ammoniac, that they should hitherto have refused to associate themselves as solids with water; while alum, soda, and the "vitriols," white, green, and blue, combine with water and form crystals of such beauty; to me of such extreme interest because in their faces and edges, as in those of other and anhydrous crystals, nature for once makes use of planes and straight lines?

It has been my good fortune to have been able, to some extent, to wipe out this line of demarcation, to establish continuity; to prove, in short, that all salts whatever, which are soluble in water, are able to combine with it in definite weight-ratio to form solid crystalline bodies. I do not doubt but that we may consider the number of known definite compounds to have been thereby at least doubled.

The formation of these new solid water-compounds may perhaps be best approached by studying the phenomena which take place when any salt solution is cooled. Let us consider a boiling saturated solution of saltpeter. Take it from over the lamp, and let it cool. A certain quantity of the salt separates out, but the crystals are free from water. Cool it down to 0° C., more anhydrous saltpeter separates; but at 0° C. it is still rich in saltpeter, and is, of course, saturated at that temperature. What takes place if we go on cooling

below $0^{\circ}\text{C}.$? If pure anhydrous saltpeter were to go on separating out until it were all out, there would be left at some temperature below $0^{\circ}\text{C}.$ pure liquid water—an impossibility. If, on the other hand, only pure ice were to separate out, we should get at last anhydrous saltpeter liquid below $0^{\circ}\text{C}.$: this is equally impossible. What actually does occur is this—anhydrous saltpeter goes on separating out until the solution has acquired a certain degree of weakness (11.20 per cent.), and this stage is reached at a certain temperature below $0^{\circ}\text{C}.$ (-2.6). When still more heat is withdrawn, the temperature refuses to sink further, and the remainder of the solution begins to solidify, and continues to solidify at the temperature and with the composition it has reached until the last drop is solidified.

If, again, we begin with a very dilute solution of saltpeter, say one containing 2 oz. of saltpeter in 98 oz. of water, it is well known that such a solution requires to be cooled below the freezing point of water before solidification begins; and the differences of opinion which have prevailed as to whether pure ice or “impure” ice is separated in such cases arise apparently from the circumstance that solutions of different strength have been examined. From our solution, pure ice is separated at a little below $0^{\circ}\text{C}.$ And as the temperature falls, more and more ice separates out, thus enriching the remaining solution. But this cannot go on indefinitely, for if it did so we should have at last anhydrous saltpeter liquid at some temperature below $0^{\circ}\text{C}.$ The enrichment goes on as the temperature falls, until the same temperature and the same composition are reached as were reached in the case of the impoverishment of the saturated solution by the withdrawal of the saltpeter. And now again the temperature ceases to fall, the salt solution ceases to change its composition, the water and saltpeter solidify together at the same temperature and in the same ratio as they did before, until the last drop is solid.

What manner of body is this which is thus formed? A solid, of crystalline form, consisting of water and saltpeter in fixed ratio, and of constant freezing and melting points. A hydrate obviously, and because it can only exist in the solid form below the freezing point of water, we may call it a cryohydrate.

Thirty or forty of the most familiar soluble salts have been examined in a similar manner and with similar results. Each combine with a certain proportion of water at a certain temperature below zero C. The proportions are different with different salts, and so are the temperatures of solidification, and at present I can only see indications in a few cases of generalizations connecting the chemical compositions with the temperatures.

The Table A and Diagram B now nearly completely explain themselves.

TABLE A.—Shows (1) The CHEMICAL FORMULA of the SALT; (2) The LOWEST TEMPERATURE to be got by mixing the SALT with ICE; (3) TEMPERATURE of SOLIDIFICATION of the CRYOHYDRATE; (4) MOLECULAR RATIO between ANHYDROUS SALT and WATER of its CRYOHYDRATE (Water-worth); (5) PERCENTAGE of ANHYDROUS SALT in CRYOHYDRATE.

(1) Formula of Salt.	(2) Temperature of Cryogen	(3) Temperature of Solidification of Cryohydrate.	(4) Molecular Ratio or Water-worth	(5) Percentage of Anhydrous Salt in Cryohydrate.
	°	°		
CaCl ₂	- 33	- 37	11·8	36·45
NaBr	- 28	- 24	8·1	41·33
NH ₄ I	- 27	- 27·5	6·4	55·49
NaI	- 26·5	- 28	5·8	59·45
KI	- 22	- 22	8·5	52·07
NaCl	- 22	- 22	10·5	23·60
SnCl ₂ + 6H ₂ O	- 18	- 17	22·9	27·57
NH ₄ SO ₄	- 17·5	- 17	10·2	41·70
NH ₄ Br	- 17	- 17	11·1	32·12
NH ₄ NO ₃	- 17	- 17·2	5·72	43·71
NaNO ₃	- 16·5	- 17·5	8·13	40·80
NH ₄ Cl	- 16	- 15	12·4	19·27
KBr	- 13	- 13	13·94	32·15
KCl	- 10·5	- 11·4	16·61	20·03
K ₂ CrO ₄	- 10·2	- 12	18·8	36·27
BaCl ₂ + 2H ₂ O	- 7·2	- 8	37·8	23·2
AgNO ₃	- 6·5	- 6·5	10·09	48·38
Sr ₂ NO ₃	- 6	- 6	33·5	25·99
MgSO ₄ + 7H ₂ O	- 5·3	- 5	23·8	21·86
ZnSO ₄ + 7H ₂ O	- 5	- 7	20·0	30·84
KNO ₃	- 3	- 2·6	44·6	11·20
Na ₂ CO ₃	- 2·2	- 2	92·75	5·97
CuSO ₄ + 5H ₂ O	- 2	- 2	43·7	16·89
FeSO ₄ + 7H ₂ O	- 1·7	- 2·2	41·41	16·92
K ₂ SO ₄	- 1·5	- 1·2	114·2	7·80
K ₂ Cr ₂ O ₇	- 1	- 1	292·0	5·30
Ba ₂ NO ₃	- 0·9	- 0·8	259·0	5·30
Na ₂ SO ₄ + 10H ₂ O	- 0·7	- 0·7	165·6	4·55
KClO ₄	- 0·7	- 0·5	222·0	2·93
Al ₂ (NH ₄) ₂ SO ₄ + 12H ₂ O	- 0·4	- 0·2	261·4	4·7
HgCl ₂	- 0·2	- 0·2	450·0	3·24

In Diagram B are shown, as well as the cryohydrates (which are the points of reflexure, or lowest points of each curve), the temperatures at which various salts of various strengths (*a* left-hand branches) give up ice and (*b* right-hand branches) give up salt.

Let me only remark concerning these ratios of Table A, that those bodies at the bottom of the list are nearly pure ice, and yet by the generalization of continuity they are bodies of similar composition to those at the top of the list which are well within the limits of chemical ratio. One is tempted to look upon these ratios as being brought about not by the same saturating capacity as determines

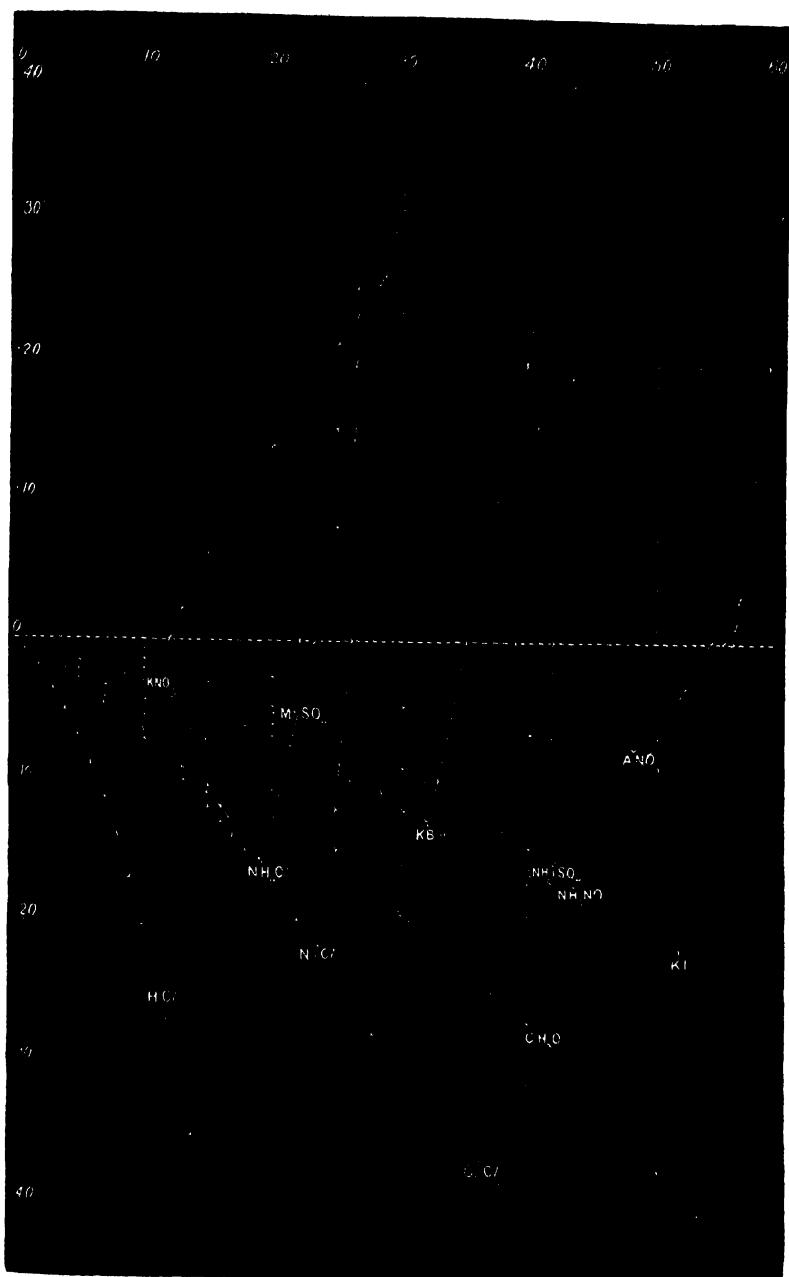


DIAGRAM B.

elementary union, but by a kind of crystallographic relationship, of which I can say no more because no more is known.

Very palpable evidence of what we may in this generation call physical relationship as distinguished from chemical relationship, is shown in the composition of innumerable minerals, and notably in the water quantity of various silicates, the composition of which can only be reconciled to ordinary chemical ratio by the greatest licence in arithmetical manipulation. I say, "in this generation," for haply the time practically predicted by Berthollet at the beginning of the century cannot be remote when the barrier between the two sciences will vanish.

Is it likely that so numerous and interesting a class of bodies as these cryohydrates should be mere creatures of the physical laboratory, and be without a function in nature? I trow not. They affect the composition of polar ice as follows.

Although sea water has no maximum density, and therefore ice can be formed anywhere in its mass, yet it loses heat mainly from the surface, and it is there that ice is chiefly formed. If the fall of temperature be gradual, the crystals of pure water which solidify are for the moment surrounded by cold sea water deprived of a portion of pure water, that is enriched sea water—a stronger brine. This sinks and diffuses, and gives place to fresher sea, which in its turn yields pure ice. By gravity and osmose, in time, the pure sea is renewed in the region of gelation, and pure ice results. But if the loss of heat be sudden and considerable, the salts of the sea are fixed as cryohydrates with the water, and so perpetuated *in situ* according to the temperature at which their cryohydrates solidify. And I should expect that paleocrystic ice formed from the freezing-sea would contain the metals sodium, magnesium, and calcium in a different relative proportion to that in which they exist in the sea water. Be this, however, as it may, it is clear to me that no theory of ocean circulation can be complete which does not take into account the formation of cryohydrates in the polar regions.

These compounds of salts with water have both a great use in many a familiar operation, and a great significance in many a familiar phenomenon. With regard to their use, I need only mention the fact, that it is clear that by their means we can attain to and maintain with absolute constancy many definite temperatures below 0° C. For a body plunged into a melting or solidifying cryohydrate will be maintained at a temperature as constant as that of melting ice or freezing water.

With regard to their significance, they give us a complete key to the hitherto closely concealed *rationale* of freezing mixtures or cryogens made by mixing ice or snow with various salts. For the degree of cold which can be reached on mixing a salt with ice can never exceed in lowness the temperature at which the cryohydrate solidifies, because the consequent solidification of the cryohydrate would furnish heat. Nay, more. Since of all ratios between

the salt and the water that of the cryohydrate demands the lowest temperature for solidification, the liquid portion of a freezing mixture can neither be stronger nor weaker than the cryohydrate, it is the cryohydrate and the slightest further loss of heat causes solidification. Look now at columns (2) and (3) of Table A, and you see how closely parallel, how, indeed, within the limits of experimental error, identical are the two series of numbers.

By cooling a thick slab of glass in a freezing mixture, and dropping upon it various salt solutions, I show you now a few cryohydrates in the act of solidification.

I may mention that not only metallic salts, but crystalline solids, of organic and inorganic origin form similar cryohydrates. Amongst the most interesting of these are the cryohydrates of alcohol and ether. The latter contains a large proportion of water, and its temperature of solidification is so little below zero C. that I can show it you. Solidified in a test tube, and removed therefrom, it forms a white crystalline rod, like a candle. The ether burns away when a light is applied to one end, and, by its non-luminosity, clearly illustrates the generalization of Dr. Frankland, that, other things being the same, a cold combustible burns with less luminosity than a hot one.

Let me here turn for a moment to the comparison between the effects of heat and cold upon salt solutions, and notice how closely parallel are the two series of phenomena.

Compare the decomposition of a salt solution by the loss of heat with the decomposition by gain of heat when such a solution boils. And in instituting this comparison, we must bear in mind how much more sensitive to variation in pressure is the boiling than the solidifying point.

And before quitting this part of the subject, I may call to mind

(1) A solution poorer than the cryohydrate loses heat; ice is formed.

(2) This goes on until the proportion of the cryohydrate is reached, the temperature falling.

(3) The cryohydrate may be reached by freezing out ice from a weaker solution, or by any other withdrawal of water.

(4) When ice separates from a liquid, it remains in contact with the liquid, and endeavours to redissolve therein.

(5) When by the separation of ice the proportion of the cryohydrate is reached (nearly independent of pressure), ice and the salt separate simultaneously.

(1) A solution poorer than that saturated at a given temperature receives heat; vapour is formed.

(2) This goes on until saturation is reached, the temperature rising.

(3) Saturation may be reached by evaporation, boiling, or any other withdrawal of water.

(4) Vapour separated from a liquid is removed from the field of contention, unless the liquid be enclosed with the vapour.

(5) When by the separation of vapour the proportion of saturation is reached (very dependent upon pressure), vapour and the salt separate simultaneously.

(6) The two bodies (ice and the salt) being crystallizable solids, unite to form a crystallizable cryohydrate which exhibits a constant gravimetric composition.

(7) A cryohydrate in the act of solidification shows identity of composition between the solid and liquid portions. The temperature of solidification is constant.

(6) One being a solid and the other a vapour, they do not unite, but in their separation preserve a constant gravimetric ratio under like conditions of pressure.

(7) A saturated solution, when boiling, shows the same ratio between the vapour formed and the salt precipitated as exists between the liquid water present and the salt it holds in solution. The temperature of boiling is (under like pressure) constant.

the fact that we find amongst the phenomena of igneous fusion facts perfectly analogous with those which we have been studying. Thus, in Pattinson's process for the desilverizing of lead, the mass containing a small percentage of silver is melted and gradually cooled, lead (ice) separates out in almost perfect purity, the temperature sinks, and more and more lead is separated, until, as Dr. Percy informs me, a two and a quarter per cent. of silver lead alloy, a pyro-plumbide (a cryohydrate), is reached.

Lastly, let us reflect upon the solidification of water in jellies, and its attitude towards colloid bodies.

My illustrious teacher Graham, in a series of researches which have perhaps never been surpassed for philosophical insight, showed how all matter is divisible into two great classes, crystalloid and colloid. He proved that a crystalloid body penetrates through a colloid without essential obstruction. The colloid and crystalloid have no grip on one another. And quite in accordance with Graham's views I find that, although gum-arabic is far more soluble in water than table salt, we totally fail to make a freezing mixture with gum and ice or snow. And inversely, when a strong solution of gum or glue is cooled, the temperature cannot be brought below 0°C . until the whole of the water has been separated as ice. This being so, we ought also to find that the presence of gum or glue in water does not raise its boiling point, as do the presence of crystalline salts. Experiment shows us that the boiling point of water is really and considerably lowered, so that if, for instance, I remove the atmospheric pressure from two vessels slightly warmed, the one containing 50 per cent. of gum and the other pure water, the gum solution is the first to boil.

In the series of barometer tubes on the table, whose images I throw on the screen, you have (1) an ordinary barometer, (2) a similar barometer with a crystal of alum in the vacuum, (3) with a saturated solution of rock salt, (4) with water, (5) with a morsel of size, and (6) with a 50 per cent. solution of gum-arabic. It is observed that the depression of the mercury, which of course measures the vapour tension, is in the order mentioned. The solid water of crystallization leaves the alum, but is partly restrained by the affinity of the residue. The saturated salt solution again, but more feebly, restrains the

water, while the gum and size do not restrain the vapour tension of the water at all ; they have no grip on the water.

Even through the colloid caoutchouc, of which the toy air-balls are made, water penetrates with marvellous facility. The one on the table, which weighs now about 700 grams, weighed 750 grams only a few weeks ago. It has been losing 0.06 grams per hour with remarkable regularity. And I suppose, if we could see the structure of a jelly, we should find it to consist of a network of solid fibres hampering the motion of the crystalloid liquid among them ; or of cells of solid elastic matter, containing liquid such as the mass of cells on the table.

The hour is up, and I must end. My task will not have been essayed in vain if I have brought forward evidence that, in the philosophy of the simplest things, yet much remains to be disclosed. Far from me the thought of undervaluing the labours of those who from time to time enrich science with hundreds of new substances of complex composition. On the contrary, I admire, I am grateful to them for their successful efforts ; for I am thoroughly assured that it is by the comparison of terms of series, which terms stand apart from one another by almost imperceptible differentials, that the great integral curves of natural generalizations can be traced out. And yet I say, and earnestly maintain, that in the philosophy of the most familiar properties of the most familiar things, there are, as it were, lying at our very doors, vast and unexplored regions ; meads brightly blooming with the unplucked flowers, and orchards mellow with the ungarnered fruits of natural truth.

[F. G.]

Friday, February 23, 1877.

SIR W. FREDERICK POLLOCK, BART. M.A. Vice-President,
in the Chair.

JOHN FLETCHER MOULTON, E-q. M.R.I.

Matter and Ether.

ALL are familiar with the process by which the discovery of the laws that govern phenomena is effected. Close study of various instances of some one phenomenon, with their general likeness and their individual peculiarities, leads; either by the slow process of trial and error or by some happy guess, to the discovery of the law to which the observed variations all conform. When this is once ascertained, the whole group of phenomena fall into harmony, and instead of a mass of separate observations, science seems but the exemplification of a single law. This step in the simplification and unification of nature taken, the human mind is free to seek further conquests. But great as is the advance made by such a step, the mind cannot rest content with it. The dry mathematical expressions which we know as the laws of nature, are soon felt to assuage scientific curiosity to a very imperfect degree. No sooner have we discovered the law that governs any set of phenomena, than we are irresistibly drawn to ask the question, How comes it that this is the governing law? of what set of hidden causes is it the outcome? And thus we are led to seek for the mechanism of nature and to find the physical causes of its laws. Nay, we go further; we cannot be content till we discover the nature and properties of the subject matter of its phenomena, and can deduce from these the previously discovered laws as necessary consequences. And the complete realization of one part, at least, of this search, is not beyond the bounds of possibility. It probably will some day be known to the human race that the whole of nature is but the manifestation of a very few distinct physical existences, possessed of known properties of so simple a kind and so universal in their presence that experience can never enable us to analyze them farther. The possible forms assumed by these elements will be deducible from their properties; and the more complex laws that will regulate the behaviour of the resulting substances, will be problems determinable from their known structure. Thus all nature will be theoretically the resultant of the interaction of known agencies, and the solution will be complete, even though the stupendous difficulties of the analysis

necessary to deduce the laws of even the more simple phenomena from the properties of these elements should compel the men of that far distant future to arrive at laws by induction from experiment, just as we do now already in the simplest of all sciences—astronomy. In this science, the phenomena of which are due to only four laws, each of which is capable of statement in most simple terms, the complexity of the analysis well-nigh drives astronomers to abandon calculation for observation, in the more delicate refinements of accuracy in which they indulge. Similar considerations will always operate to keep distinct the sciences that deal with distinct classes of phenomena, long after it has become a recognized truth that they are all the more or less complex manifestations of some few known elemental, physical existences. And certainly no considerations of the limits of possible success can avail to destroy the fascination of researches into the ultimate constitution of the existences of which nature is built up—the minute anatomy of the universe.

But although investigations of this nature are so interesting, and promise not only success, but success of the highest order, and although the interest of the research is common to the devotees of every science, inasmuch as it deals with that which underlies them all, it is most remarkable that so little advance has been made in this direction. And not only is it the case that we are compelled to admit that our ignorance of the ultimate constitution of matter is well-nigh as dense now as it ever was, but if we examine the attempts at solving the problem, hitherto made, they strike us at once as having the strangest characteristics. While in most of the other regions of research the results of all investigators have a certain family likeness, and the theories they propose—though perhaps mutually exclusive—have many points in common, yet here we find that the different solutions proposed have the wildest dissimilarity, and many of them present so fantastic an appearance, that it is difficult to believe that they are the productions of the sober investigators whose names they bear. We are too apt to pass lightly over the lesson taught us by the contemporaneous existence of the corpuscular and the undulatory theories of light. That two theories so diametrically opposite in nature, hypothesizing such utterly different constructions and properties of matter, could at a time not so very long past have been considered as possessing tolerably equal claims to acceptance, opens up a vista of ignorance as to the ultimate constitution of matter which is very humiliating. Nor will it suffice to say that those were the days when true science was in its infancy. Though the dispute between the two theories of light was speedily settled by the complete defeat of the corpuscular theory, and our ignorance of the real mechanism that produces and transmits light was rendered thereby less total—in fact we may say that it was so far dispelled that only those capable of thoroughly understanding the subject, can feel the difficulties and imperfections of the accepted theory—yet similar struggles are still going on in other kindred subjects, and for them

no such excuse can be pleaded. Take, for instance, electricity and magnetism. Our knowledge of their phenomena is extraordinarily wide; such a book as Wiedemann's 'Galvanismus' shows an accumulation of observations on one simple branch of the subject that can scarcely be paralleled in any other science. Yet if we look at the rival theories as to the nature of electricity, and its connection with matter, they seem so grotesque and so dissimilar—so like mere guesses in short—that we can scarcely help fancying that we are back in the days of Lucretius, when the best qualification for being a philosopher was to be an imaginative poet. And indeed in fertility of imagination, the authors of such theories as those to which we are referring seem not unworthy rivals of the Roman poet, and they make similar demands on our powers of belief. Weber and Ampère's ideas of magnetism being caused by each molecule of matter having its own special electric current circulating round it everlastingly; Poisson's idea that it is caused by each molecule being permeated by two mutually neutralizing fluids, capable of being separated by external attraction, but incapable of being removed from the molecule; the rival theories of two fluids, of one fluid, and of no fluid, in electricity, the numerous theories as to the nature of the luminiferous ether and its relation to matter, and the vortex theory of atoms, suffice to show that no effective check has as yet been placed on the free use of the imagination in this department of research, and seem to give some colour to the suggestion that the intolerance of credulity, professed by men of science, is easily relaxed by them in favour of their own pet theories.

The chief and immediate cause of this is not far to seek. Any attempt to arrive at the hidden mechanism which causes a phenomenon, must be a direct reflex of the knowledge and the ignorance of the age in which it is made. Let us take the case of some ingenious machine performing some known operations. If a person wholly ignorant of mechanism, save so far as the objects of common life teach it to intelligent observers, were to attempt to solve the problem of its construction, he would seek for some arrangement of levers or other mechanical appliances of the simplest and most elementary nature, which would give the desired result. If a mechanician were to apply himself to the same problem, he would have present to his mind all the refinements of mechanical science, and would probably arrive at a solution, no portion of which would resemble the one composed of the simpler elements, while his might in no respect resemble that which would be arrived at by one who, in addition to possessing a knowledge of mechanism, was also a skilled electrician. Each of the solutions would consist of the elements which the experience and knowledge of the maker enabled him to use, and there would be no probability of any of them representing the actual construction of the machine in question, unless the artifices used in its construction were such as were known to some of the persons who were thus attempting to reconstruct it. Just so is it with the attempts we make to arrive

at the mechanism of nature. They are charged to the full with our ignorance. If we happen to be acquainted with structure similar to the actual structure sought for, then success is possible, and some discoverer will in all probability arrive at a close approximation to the real state of things. If we do not, then all our efforts will but lead us to the discovery of a *possible* mechanism—one which might cause the phenomenon, but which is not the one which actually does cause it; and with this we must rest content, till in some way or other our knowledge of possible elements of construction is widened, when we may return again to the problem and find a new solution, which may in its turn have to be replaced by future ones. Take, for example, the question of the structure of matter. Matter was known to move with little or no resistance through the ether, to attract other matter, to be capable of great complexity in its nature, inasmuch as the light proceeding from elements, when in a state of incandescent gas, shows that they are capable of a large number of fundamental vibrations. To explain all this many most ingenious hypotheses were devised, both as to ether and matter; molecules or atoms were viewed as complex arrangements of parts vibrating or revolving under their mutual attractions. Ether was made an imponderable. Space was filled with ultra-mundane corpuscles, which, by their perpetual rain on all masses of solid matter, caused the phenomenon of gravitation. At length Helmholtz discovered vortex-motion. Vortex-rings were found to move with little or no resistance in the medium, whether fluid or gaseous, in which they were formed; they were sensible of the presence of one another though not in contact; they were capable of being made to have the most intricate forms, and to take up the most complicated systems of vibrations. Instantly a vortex-theory of matter was devised, which has very much to recommend it, and which is at present the one in highest favour. But just as it was only rendered possible by Helmholtz's discovery of the new form of motion after which it is named, so it may in its turn have to give way to other theories which enlarged knowledge shall have enabled us to suggest.

The difficulty at once suggests itself, that if we admit that these theories as to the actual mechanism of nature are so intimately dependent on the state of the ignorance or knowledge in which we are when they are framed, how can it be right to attach any credence to them? How can we believe a theory at the same time that we admit that it will be probably displaced by another and a different one which will have at least as high claims to our belief? Science would at once lose all claim to be called the strictest school of belief, if it countenanced any such moral gymnastics as a belief which could thus co-exist with disbelief. And yet so great is the assistance derived from a well-constructed theory as to the mechanism producing phenomena, that she cannot afford to allow all efforts at solving such problems to be delayed until there comes a stage of such perfect knowledge, that the mind might claim to be capable of pronouncing on them with certainty—if indeed such a time could ever come. So she

boldly faces the difficulty of which we have spoken—the difficulty of showing any other choice open to scientific men, than either to be credulous or to be timid—by distinctly recognizing a class of scientific fictions, or, as they are usually called, hypotheses. These are theories as to the mechanism of nature which, either completely or to a great extent, account for some set of phenomena, and which therefore, so far as our knowledge goes, may correctly describe the whole or some part of the actual cause of the phenomena, i. e. the mechanism that produces them.

Nothing is more important in scientific thought than to distinguish between these hypotheses and laws. The discoverer of laws has nothing to do with actual causes. He only notices and formulates connections and relations between phenomena, and these formulations are laws. So far as the law is concerned, it is immaterial whether the one of two connected phenomena is the cause or the effect of the other, or whether the relation between them arises from their being both connected with a third phenomenon; the law is equally true in all cases. So long as the induction which has led to it has been duly and carefully performed, it is true and will never be displaced or superseded, however mistaken were the ideas which its framer possessed of the nature or causes of the phenomena to which it relates. Newton was quite right when he said, *hypotheses non fingo*; for the portion of his great achievements to which he was referring consisted in the demonstration of the existence of certain laws, and not in the explanation of their causes. But he, as well as all other great men of science, when the right time came, was ready to frame hypotheses, to start these scientific fictions, which were to be thankfully received, studied, tested, respected, worked from, and in short, everything but actually believed in. And he least of all would have, on the one hand, despised these tentative solutions, or, on the other hand, lightly believed in their truth. The whole of his work shows that he appreciated the full value of hypotheses, a value which it is difficult to express clearly, but which every learner or teacher of science feels only too keenly. For, without some guiding idea as to the nature and causes of phenomena, the mind is very sluggish in devising good methods of investigation; but so soon as a good hypothesis has been formed, it is so suggestive of fields of research and of experiments, that, whether it be true or false, there follows an immediate and rapid increase of knowledge. For a hypothesis may be a good one without being a true one. It may render the greatest assistance to the mind, it may be so well chosen that it accounts for kindred phenomena, not known at the time when it was first suggested, it may lead to the discovery of new laws, and it may enable calculations to be made which are of the highest value, and yet it may turn out to be radically false. Even the theory that heat was an imponderable fluid, might put forth a strong claim to our gratitude for the assistance it gave to early discoveries. To be thus useful for a time, it is not necessary that the assigned mechanism should be the

true one, but only that the laws that result from its structure should closely correspond with the more potent of the laws that actually direct the observed phenomena. And just as this is all that a hypothesis need do, so is it all that its success entitles us to believe that it is doing; and the true scientific attitude of mind towards hypotheses is to recognize them as describing causes which would produce results similar to those observed, and which, if not truly representing the mechanism which actually causes the results, at all events would produce results governed by the same laws.

How then are we to take the further step of selecting from amongst those rival hypotheses, each of which professes to give some mechanism able to produce a particular set of phenomena, the one that actually represents the mechanism by which the phenomena are in fact produced? This is the most serious and the most difficult step in discovery. And yet, at first sight, considering how complex are the phenomena that have to be explained, it would seem that any theory that succeeded in accounting for even a portion of them must be very near to the truth; and it is so usual to consider that this is the final and sufficient test of the claims of a hypothesis, viz. that it should suffice to account for the phenomena, that when they are very complex it is often considered a more than sufficient test, and the hypothesis is accepted in spite of its being in many respects undeniably deficient. But, in fact, so soon as we begin to apply ourselves seriously to the problems of the constitution of matter—the hidden mechanism of nature—we are forced to abandon in great measure all such ideas. For we find that we have no true measure of complexity. From one single simple law will follow the most various and complex results, and hence any mechanism so designed as to exemplify in its results the working of that single law would, under such a canon as the one just referred to, be able to claim as evidence of its truth all the complexity which follows from that law. Yet such evidence would equally avail to support the claims of any other mechanism, whose results similarly obeyed that law, and of such mechanisms there might be many. This has been often exemplified in the history of science. The truth of a hypothesis has appeared to be sufficiently demonstrated by the manner in which it fully accounted for complex phenomena, and it has been accepted as a physical truth on such grounds, until some other hypothesis has been shown equally capable of accounting for them; and the success of both has been subsequently traced to their alike leading to results that were obedient to some one fundamental law, to the working of which the whole of the observed complexity was due. In the history of such deep-reaching principles as that of the Conservation of Energy this has been a common occurrence; but other instances are not wanting. After Sir W. R. Hamilton had deduced theoretically from Fresnel's Theory of Light, that in biaxial crystals there must be internal and external conical refraction, and their existence had been thereupon experimentally demonstrated by Dr. Lloyd, one might well have fancied that the accuracy of so remarkable a prognostication was sufficient

to establish Fresnel's Theory in all its details. Yet a theory framed by Cauchy, which, though in many respects similar to Fresnel's Theory, is yet in fact wholly irreconcilable with it, was subsequently found to account equally for the phenomena; and it is probable that any theory of undulatory transmission in a non-isotropic medium might be made to do the like. In fact, we can express in abstract language the weakness of the canon which would make the acceptance of a theory follow from its success in explaining complex phenomena, by saying that to render the canon a good one, complexity must be measured, not by the apparent intricacy of the resulting phenomena, or the apparent difficulty of accounting for them, but by the number of independent laws by which the phenomena are governed, and which are successfully accounted for by the proposed mechanism. And as we are seldom in a position to pronounce on the question of the independence of the laws that govern a set of phenomena, i.e. as to whether they are all traceable to a very few fundamental laws or not, we are seldom able to estimate the complexity of those phenomena in the way that would alone justify us in taking it as sufficient warrant for the acceptance of a successful hypothesis.

Nor is this the only one of the well-tried and approved canons of discovery that fails us when we are engaged in researches in the unknown land of the ultimate constitution of that of which the universe is composed. There is no principle which is more constantly present to the mind of the scientific investigator in his search for the causes of phenomena than that of simplicity. Wondrously complex as are the processes that are going on all around us in nature—so apparently complex that the untaught mind has in all ages sought to ascribe them, in a greater or less degree, to consciousness and volition resident in the things themselves, or in beings possessing the power to direct them—science has so often found that these highly complex results come from the very simplest causes, that the investigator expects to find simplicity in his results, and naturally inclines to believe that explanation to be the true one which accounts in the most simple manner for the observed phenomena. This has been advanced by some persons almost to the dignity of a law of thought, and the mind is considered by them to be constrained to believe in the truth of the simplest hypothesis that explains a set of phenomena to the exclusion of all more complex ones.

It is not very easy satisfactorily to account for the undoubted value of this canon, viz. that the simplest hypothesis is probably the true one. That there can be any truth in it in its abstract form (as is generally understood) is not probable. There is no reason to think that nature has any preference for simplicity over complexity, if indeed it is possible to attach any meaning to such phrases. The deeper our knowledge becomes, the greater the complexity that confronts us, and the fainter our hope of finding that the ultimate solution will be a simple one. It is probable that much of the value of the canon arises from the fact that the simpler hypothesis will in general be the one that supposes the concurrent action of the fewest

independent causes ; and it is, of course, more probable that a smaller number of independent causes should co-operate than that a larger number should do so. But the value of the canon mainly lies in the view which the mind instinctively takes of simplicity. That is to us simple which is the result of means and processes to which we are thoroughly accustomed, and with the results of which we are fully familiar. Operations the most complex in their nature are often felt to be simple, and scarcely to need any explanation, solely because they are so common. It seems, for instance, almost superfluous to invent elaborate mechanism to account for such simple phenomena as evaporation or weight. And thus a hypothesis which is felt to be simple is usually one which traces the phenomena to the action of causes with which we are very familiar, i. e. which are constantly at work around us, and which are therefore just the causes that are the most probable.

From such considerations we at once see how useless must the canon of simplicity be to us when investigating the ultimate constitution of the materials of which the universe is built up. For, in the first place, we have little or nothing to guide us as to the probability of the concurrence of different causes in this unknown region, and secondly, a thing which is of infinitely greater moment, we are absolutely ignorant (save in one or two isolated points) of the types of structure and action that we may expect to find commonly exemplified therein. For in seeking to determine the ultimate constitution of matter and ether, and of all that directly or indirectly acts upon them, we are going beyond all the phenomena with which we have been rendered familiar by observation, whether general or special, and we are occupied in ascertaining the mechanism by which matter and ether are enabled to produce the phenomena we see. Now, of this we have no previous experience, and it cannot be too distinctly kept in mind that where there is no experience there is absolute ignorance. In the world around us we see only the aggregate results of infinitely numerous separate actions, none of which are simply cognizable by our senses or our instruments. Every experience of matter that we have in mechanics is of matter acting in masses. Chemistry and physics give us certain phenomena, caused doubtless by a more intimate action of matter upon matter, but the results are only known to us in gross ; and even if we assume that the process is uniform throughout, it is only the result of that process that we see, and its nature is wholly concealed from our view. Similar remarks apply to the other branches of science. Nowhere do we get any direct information as to the nature or details of these processes, or as to the mechanism by which they are rendered possible, and thus we nowhere get any knowledge of the types of mechanism that we may expect to find at work. It is true that in all action of matter upon matter we see that certain laws are universally obeyed. But all that this enables us confidently to enunciate is, that the nature of matter must be such that when matter acts upon matter in appreciable quantities, such and such laws obtain. We are not even justified in asserting that the most

universal of these laws must necessarily hold good in the case of the separate actions of which the aggregate is made up.* Still less are we in a position to say that one hypothesis is to be preferred to another, because it hypothesizes only such types of structure or action as we are familiar with in our experience of the world of visible phenomena. It is scarcely too much to say that at present our ignorance of the ultimate constitution of matter is such that no one suggested structure ought to be viewed by us as being in itself more simple or more probable than another.

Unable then to use these canons in their ordinary form, we are driven back to the truths that underlie them. It is true that we cannot rightly judge of the value of success in explaining the complex behaviour of matter as a test of the truth of a hypothesis. And it is also true that we cannot directly judge whether the causes we propose to assign for that behaviour are probable ones. But out of the combined effect of the two there arises a third canon of the highest value, specially adapted to meet the peculiar difficulties of the task. It may, perhaps, be expressed by saying that the probability of the truth of a suggested hypothesis, as to the constitution of matter or the nature and mode of transmission of its actions on other matter, is measured by the dissimilarity of the phenomena explained by it. So long as the hypothesis satisfactorily accounts for but one class of kindred phenomena, no matter how complex they may be and how satisfactorily it may account for them, its truth must still remain in doubt, inasmuch as from our ignorance we are unable to say how much is denoted by that success, in other words, how far such success may be due to these phenomena being necessary consequences of but very few laws, or even of a single one. But if the same hypothesis explains phenomena of a wholly different character to those which suggested it, and which so far as we can judge have no direct connection with them, then we are justified in accepting the hypothesis as a genuine contribution to our knowledge of nature.

This will be rendered clearer by an example. Take as an instance what is probably the most successful attempt that has yet been made to penetrate the darkness that surrounds the constitution of matter. Long ago, in order to explain the phenomena of combining proportions in chemistry, the hypothesis was framed that every element or chemical compound consisted of small atoms or molecules of definite size, constitution, and weight, and that the process of chemical combination consisted in the building up of new compound

* This is no idle refinement. No law would seem to be more absolutely without exception than that heat of itself tends to pass from a hot body to a cold body, i. e. that heat tends towards an equalization of temperature. Yet this has been shown to depend in some instances rather upon the law of averages than on the fundamental laws of energy, and to be inapplicable to the action of single molecules; and it is not impossible that we might be driven to take a similar view of such a law as that of the conservation of energy, though, fortunately, nothing as yet points to this, and it would, therefore, be unscientific to increase the difficulty of investigation by making such a hypothesis until it shall be found that there are good grounds for doing so.

It is not, however, so much in relation to other elements that vanadium is interesting, as by virtue of the remarkable properties which the metal itself possesses. Thus the lowest stage of oxidation which the element can assume, viz. V_2O_3 , is a powerful reducing agent, bleaching indigo by reduction almost as quickly as chlorine does by oxidation. On allowing the solution thus bleached to stand, the hypovanadous salt at once takes up oxygen from the air, and indigo blue appears again. On the other hand, the highest oxide V_2O_5 parts with its oxygen readily, and is easily reduced by organic matter to a lower oxide; acting in this respect like the highest oxide of chromium CrO_3 .

This property of vanadic acid enables this substance to be employed in photography.* If gelatine be mixed with sodium divanadate, and the film unequally exposed to light, the portions strongly insolated become slightly less soluble in warm water than the non-exposed portion, so that it is possible to print from such a film. Again, if paper which does not contain any animal size is coated with a solution of sodium ortho-vanadate and then exposed to light, the portion insolated assumes a dark tint dependent upon the length of exposure and the strength of the solution employed. If the paper thus prepared be immersed, after exposure, in a solution of silver nitrate, the colour in the exposed part instantly changes to a dark brown or black colour, doubtless due to the reduction of the silver salt by the vanadous compound formed in the paper. Paper thus prepared may be used for photographic printing. The unexposed portions of the print are in this process coated with yellow silver ortho-vanadate; but this can be completely removed by ammonia or by sodium hyposulphite. Silver ortho-vanadate is capable of forming a latent image, like the chloride or bromide, and this may be developed by the ordinary ferrous developer. Two or three minutes' exposure to sunlight is needed. In the development little or no silver nitrate must be present.

By far the most important and interesting application of vanadium is, however, that recently suggested for the preparation of a permanent black which is now largely coming into use amongst dyers and calico printers, and is already extensively employed as a permanent marking ink.

Of the commercial value of a permanent rich black dye it is difficult for the uninitiated in such matters to form an idea. Suffice it to say that it is very great. We must, however, remember that this application of vanadium is only in its infancy, and whether the vanadium black will realize all the requirements of practice is a question which can only be settled by long and patient inquiry; still it has already so far proved a success that we may look forward with confidence to its future.

It is not at first sight easy to understand how a rare substance like

* This proposal was first made by Mr. James Gibbons in 1874.

vanadium, the price of which not long ago was 1s. 6d. per grain, and which even now cannot be obtained for less than $\frac{1}{2}$ d. a grain, can be employed for the production of a black colour, which, if not cheap and able to compete with the other common dyes, is of course useless in a practical and commercial point of view.

In order to understand the possibility of the technical application of one of Nature's rarest gifts, the history of the preparation of aniline black must be noticed. The splendid red, crimson, violet, green, and blue colours which are obtained from aniline are now universally known and appreciated, and their wide-spread manufacture serves as a striking illustration of the value of original scientific investigation. It is, however, not so generally known that not only the bright and gay colours, but also sombre browns and jetty blacks—by far the most valuable because by far the most generally used of colours—can be obtained from aniline.

In the year 1860, Mr. John Lightfoot, calico printer, of Accrington, applied to the processes of calico printing a black colouring matter which had been previously obtained in the manufacture of mauve from aniline by Messrs. Roberts, Dale and Co., of Manchester.

This black colouring matter is invariably formed when either aniline or toluidine, or mixtures of these two substances, are subjected to oxidizing actions; but in spite of several researches which have recently been published on aniline black, we are as yet unacquainted with its chemical formula, nor indeed can we say that it even possesses a constant chemical composition.

In order that a colouring matter shall be fixed or permanent, it must be fastened in some way to the fibre of the cloth. In the case of cotton this is generally effected (1) either by the precipitation of the soluble colouring matter in the fibre by means of a mordant which forms an insoluble compound termed a lake with the colour, as in madder dyeing and steam-colour printing; or (2) by the fixation of the colour by means of albumen, as in pigment printing; or (3) by the gradual oxidation and consequent precipitation of the colouring matter in the fibre, as in indigo printing. It is to this latter class of processes that aniline-black dyeing or printing belongs; for the aniline salt under the action of certain oxidizing agents passes more or less quickly from the condition of a colourless solid readily soluble in water, into that of a black amorphous insoluble powder not to be distinguished at first sight from soot. Hence if the cloth can be impregnated with the aniline and with the oxidizing agent at the same time, and if the process of oxidation can be allowed to go on in the fibre, the black will be formed and will be permanently fixed in the fabric.

Many oxidizing agents, such as chlorine, ozone, or electrolytic oxygen, have the power of transforming aniline into this black pigment. In most cases a high temperature is needed for this purpose. Thus, for instance, if aniline is heated with chlorate of sodium, and if then hydrochloric acid be carefully added, a deep black

almost solid mass is produced. In order, however, that the process may be employed in dyeing and calico printing, it is absolutely necessary to avoid high temperatures as well as the action of strong acids, because when exposed to these the cloth invariably is rotted or becomes "tender." If a mere mixture of aniline salt and chlorate of potash be heated strongly enough, the black is formed; but the heat necessary to produce the colour is sufficient, together with the hydrochloric acid which is at the same time liberated by the decomposition, to make the cloth rotten, and therefore to render this process useless.

It was found by Lightfoot that if an addition of 4 ounces of nitrate of copper solution was made to the pound of aniline and to the chlorate, the oxidation of the aniline went on at a lower temperature than when the copper salt was absent, and hence, when carefully worked, the black could be formed by this process without tendering the cloth. Certain technical objections to this process, however, soon arose; and in 1865 Lauth proposed to use the insoluble copper sulphide instead of the soluble nitrate, "by which means he prevented the deposition of copper on the "rollers" and on the "doctors" which took place in Lightfoot's process. The method thus modified has been and is now extensively used for the production of black, and the chief, if not the only, objection which can be urged against it is that the black thus obtained is not perfectly permanent, but is liable to become green when exposed to reducing agents, such as the sulphurous acid contained in the impure air of our towns. This is, however, a serious drawback, and one which those practically engaged in solving such problems have not been able to remove. So much so indeed is this the case, that it is generally believed that the property of aniline black to become green when exposed to sulphurous acid, and to return to the black when treated with alkalis, is an essential property of the substance, which may be compared with the property of litmus to change colour in presence of acids and alkalis.

That the aniline black can not only be produced in presence of copper but also, as Mr. Lightfoot showed in the year 1871, in presence of vanadium salts, and that by vanadium alone can the black be obtained of the requisite permanent character, has now been proved beyond doubt. Moreover, the quantity of the vanadium necessary in order to produce the oxidation of the aniline is about one thousand times less than that of the copper. Thus if a piece of calico be dipped into a solution of 2.5 grains of vanadate of ammonia dissolved in a gallon of water and then dried, the cloth thus prepared is capable of producing an intense black if treated with the mixture of aniline salt and chlorate. In the same way if 1 gallon of colour be made containing 20 ounces of aniline hydrochlorate, 10 ounces of chlorate of soda, and 3 grains of vanadate of ammonia, a mixture is obtained with which no less than from 20 to 25 pieces, or from 500 to 600 yards of cloth, such as that exhibited, can be thus printed of a permanent black.

In dyeing also, the vanadium will be extensively used; and in the same way only mere traces of this rare metal are requisite, whereas the copper black cannot be used for dyeing. Thus, for instance, 1 gallon of colour intense enough to dye 40 lbs. of cotton yarn black is obtained by mixing 8 ounces of aniline hydrochlorate, 4 ounces of sodium chlorate, and 8 grains of vanadate of ammonia. Cotton, wool, or silk dipped twice into this mixture and then aged, or allowed to oxidize, and "raised" in a solution of carbonate of soda, is dyed a deep rich and permanent blue black. The goods may also be allowed to steep in a bath of the above strength for three days, then well washed in warm water, or boiled in a weak solution of acetic acid, to remove any bronze colour found on the surface of the silk or wool. The permanent black is then formed, and the fibre found to be quite strong.

The part played by vanadium in the formation of the black colour may be easily explained, when we remember the ease with which the metal passes from one degree of oxidation to another; thus from V_2O_5 the highest degree, to V_2O_4 , and *vice versa*. In this way it doubtless acts, as M. Guyard has suggested, as a carrier of the oxygen of the chlorate to the aniline, being alternately reduced and re-oxidized, so that an infinitely small quantity of vanadium compound will convert an infinitely large quantity of aniline salt into aniline black, reminding one of the action of nitrous fumes in the leaden chamber.

Some time after the discovery of aniline black, Mr. Robert Pinkney, of the firm of Messrs. Blackwood and Co., of London, discovered, independently of Mr. Lightfoot, that vanadium can be most advantageously substituted for copper in the formation of aniline black; and he employed this reaction for the preparation of a permanent marking ink termed "Jetoline," of which many thousands of bottles have been sold. A few grains of vanadium—say from seven to twelve—being sufficient to produce, together with hydrochlorate of aniline and chlorate of soda, a gallon of marking ink.

The subject of the use of vanadium as a valuable dyeing agent was next taken up by the Magnesium Metal Company, of Patricroft, near Manchester, and, thanks to the unwearied exertions of Mr. Samuel Mellor, this firm have now succeeded not only in securing a very considerable supply of the rare element which occurs in the Keuper sandstone as the new mineral Mottramite, but are now in a position to produce a vanadium black for both calico printing and dyeing which is perfectly permanent. This is the more remarkable, as up to this time no aniline black made with copper has been produced in commerce which will withstand the reducing action of sulphurous acid.

As the result of a large number of experiments made with various qualities of commercial aniline, and by varying the strengths of solutions, proportions of aniline and sodium chlorate employed, and also by altering the temperature and the conditions of ageing, Mr. Mellor

has found (1) that within certain limits the purer the aniline used, the deeper and more permanent is the black obtained. (2) That there is a maximum density of colour, beyond which if larger proportions of aniline salt and chlorate are used, corresponding advantages of colour are not obtained. This maximum colour is yielded by 16 ounces to 20 ounces of hydrochlorate of aniline per gallon of colour. (3) That for the formation of a permanent black, the amount of aniline salt and sodium chlorate used for 1 gallon of colour must bear a definite relation to each other, the weight of sodium chlorate being about one-half that of the aniline hydrochlorate used. (4) That the permanency of the black depends very much upon the care and skill shown in "ageing" the cloth. If the cloth is aged in a moist atmosphere a blue-black is developed, which is very fleeting; but if aged in a dry air, and at a high temperature, a permanent black is obtained. It is also interesting to learn that for other colours also, the use of vanadium appears to be of value, as in the production of catechu browns as well as in some of the brighter aniline dyes.

It is indeed impossible to say what important technical functions this rare and hitherto unapplied substance may not fulfil. Only the other day vanadium was accounted one of our greatest chemical curiosities, and the investigation of its properties would have been thought, by the practical Englishman, to be a mere waste of time.

Now, however, we have in vanadium a new example of the value of pure scientific research, which must carry conviction even to the most utilitarian of minds.

[H. E. R.]

Friday, February 2, 1877.

SIR T. FREDERICK ELLIOT, K.C.M.G. Vice-President, in the Chair.

PROFESSOR OSBORNE REYNOLDS,

OWENS COLLEGE, MANCHESTER.

Vortex Motion.

IN commencing this discourse the author said, Whatever interest or significance the facts I hope to set before you may have, is in no small degree owing to their having, as it were, eluded the close mathematical search which has been made for them, and to their having in the end been discovered in a simple, not to say commonplace, manner. In this room you are accustomed to have set before you the latest triumphs of mind over matter, the secrets last wrested from nature by gigantic efforts of reason, imagination, and the most skilful manipulation. To-night, however, after you have seen what I shall endeavour to show you, I think you will readily admit that for once the case is reversed, and that the triumph rests with nature, in having for so long concealed what has been so eagerly sought, and what is at last found to have been so thinly covered.

The various motions which may be caused in a homogeneous fluid like water, present one of the most tempting fields for mathematical research. For not only are the conditions of the simplest, but the student or philosopher has on all hands the object of his research, which, whether in the form of the Atlantic waves or of the eddies in his teacup, constantly claims his attention. And, besides this, the exigencies of our existence render a knowledge of these motions of the greatest value to us in overcoming the limitations to which our actions are otherwise subject.

Accordingly we find that the study of fluid motion formed one of the very earliest branches of philosophy, and has ever since held its place, no subject having occupied the attention of mathematicians more closely. The results have been, in one sense, very successful; most important methods of reasoning have been developed, mathematical methods, which have helped to reveal numberless truths in other departments of science, and have taught us many things about fluids which most certainly we should not otherwise have found out, and of which we may some day find the application. But as regards the

direct object in view, the revelation of the actual motion of fluids, the research has completely failed. And now that generations of mathematicians have passed away, now that the mysteries of the motions of the heavenly bodies, of the earth itself, and almost of every piece of solid matter on the earth have been explained by mathematicians, the simplest problems of fluid motion are yet unsolved.

If we draw a disc flatwise through the water, we know by a process of unconscious geometrical reasoning that the water must move round the disc; but by no known mathematical process could the motion be ascertained from the laws of motion. If we draw the plate obliquely through the water we experience a greater pressure on the one side than on the other. Now this case, representing as it does the principle of action of the screw propeller, is of the very highest importance to us; and yet, great as has been the research, it has revealed no law by which we may in a given case calculate the resistance to be obtained, or indeed tell from elementary principles in what way the water moves to let the plate pass. Again, the determination of the resistance which solid bodies, such as ships, encounter is of such exceeding economic importance, that theory, as shipbuilders call it, having failed to inform them what to expect, efforts have been, and are still being, made to ascertain the laws by direct experiment. Instances might be multiplied, but one other must suffice. If we send a puff of fluid into other fluid we know that it will travel to a considerable distance, but the manner in which it will travel and the motion it will cause in the surrounding fluid, mathematics have not revealed to us.

Now the reasons why mathematicians have thus been baffled by the internal motions of fluids appear to be very simple. Of the internal motions of water or air we can see nothing. On drawing the disc through the water there is no evidence of the water being in motion at all, so that those who have tried to explain these results have had no clue; they have had not only to determine the degree and direction of the motion, but also its character.

But although the want of a clue to the character of the motion may explain why so little has been done, it is not so easy to understand how it is that no attempts were made to obtain such a clue. It would seem that a certain pride in mathematics has prevented those engaged in these investigations from availing themselves of methods which might reflect on the infallibility of reason.

Suggestions as to the means have been plentiful. In other cases where it has been necessary to trace a particular portion of matter in its wanderings amongst other exactly similar portions, ways have been found to do it. It may be argued that the influences which determine the path of a particular portion of water are slight, subtle, and uncertain, but not so much so as those which determine the path of a sheep. And yet thousands of sheep have been from time immemorial turned loose on the mountains belonging to different owners, and although it probably never occurred to anyone to reason out the paths

of his particular sheep, they have been easily identified by the aid of a little colour. And that the same plan might be pursued with fluids, every column of smoke has been evidence.

But these hints appear to have been entirely neglected, and it was left for nature herself, when, as it were, fully satisfied with having maintained her secret so long, and tired of throwing out hints which were not taken, at last to divulge the secret completely in the beautiful phenomenon of the smoke ring. At last; for the smoke ring is probably a phenomenon of modern times. The curls of smoke, as they ascend in an open space, present to the eye a hopeless entanglement; and although, when we know what to look for, we can see as it were imperfect rings in almost every smoke cloud, it is rarely that anything sufficiently definite is formed to attract attention, or suggest anything more important than an accidental curl. The accidental rings, when they are formed in a systematic manner, come either from the mouth of a gun, the puff of a steam engine, or the mouth of a smoker, none of which circumstances existed in ancient times.

Although, however, mathematicians can in no sense be said to have discovered the smoke ring, or the form of motion which it reveals, they were undoubtedly the first to invest it with importance. Had not Professor Helmholtz some twenty years ago called attention to the smoke ring by the beautiful mathematical explanation which he gave of its motion, it would in all probability still be regarded as a casual phenomenon, chiefly interesting from its beauty and rarity. Following close on Helmholtz came Sir William Thomson, who invested these rings with a transcendental interest by his suggestions that they are the type after which the molecules of solid matter are constituted.

The next thing to enhance the interest which these rings excited, was Professor Tait's simple and perfect process of producing them at will, and thus rendering them subjects for lecture-room experiments. Considering that this method will probably play a great part in perfecting our notions of fluid motion, it is an interesting question how Professor Tait came to hit upon it. There is only one of the accidental sources of these rings which bears even a faint resemblance to this box, and that is the mouth of a smoker as he produces these rings. This might have suggested the box to Professor Tait. But since this supposition involves the assumption that Professor Tait sometimes indulges in a bad habit, and as we all know that Professor Tait is an eminent mathematician, perhaps we ought rather to suppose that he was led to his discovery by some occult process of reasoning which his modesty has hitherto kept him from propounding.

But however this may be, his discovery was a most important one, and by its means the study of the actual motion of these rings has been carried far beyond what would otherwise have been possible.

But it has been for their own sake, and for such light as they might throw on the constitution of matter, that these rings were studied.

The most important lesson which they were capable of teaching still remained unlearned. It does not appear to have occurred to anyone that they were evidence of a general form of fluid motion, or that the means by which these had been revealed, would reveal other forms of motion.

There was, however, at least one exception, which will not be forgotten in this room: the use of smoke to show the effect of sound upon jets of air.

Also, the late Mr. Henry Deacon, in 1871, showed that minute vortex rings might be produced in water by projecting a drop of coloured water from a small tube. And his experiments, in spite of their small scale, excited considerable interest.

Four years ago, being engaged in investigating the action of the screw propeller, and being very much struck by the difference between some of the results he obtained and what he had been led to expect, the author made use of colour to try and explain the anomalies when he found that the vortex played a part in fluid motion which he had never dreamt of; that, in fact, it was the key to almost all the problems of internal fluid motion. That these results were equally new to those who had considered the subject much more deeply than he had, did not occur to him until after some conversation with Mr. Froude and Sir William Thomson.

Having noticed that the action of the screw propeller was greatly affected when air was allowed to descend to the blades, he was trying what influence air would have on the action of a simple oblique vane, when a very singular phenomenon presented itself. The air, instead of rising in bubbles to the surface, ranged itself in two long horizontal columns behind the vane. There was evidence of rotational motion about these air lines. It was evident, in fact, that they were the central lines of two systematic eddies.

That there should be eddies was not surprising, but eddies had always been looked upon as a necessary evil which besets fluid motion as sources of disturbance, whereas here they appeared to be the very means of systematic motion.

Here then was the explanation of the nature of the motion caused by the oblique vane, a cylindrical band of vortices continually produced at the front of the plate, and falling away behind it in an oblique direction.

The recognition of the vortex action caused behind the oblique vane, suggested that there might be similar vortices behind a disc moving flatwise through the water, such as are the eddies caused by a teaspoon.

There was one consideration, however, which at first seemed to render this improbable. It was obvious that the resistance of the oblique vane was caused in producing the vortices at its forward part; so that if a vortex were formed behind a flat plate, as this vortex would remain permanently behind, and not have to be continually elongated, the resistance should diminish after the plate was once set in motion;

whereas experience appeared to show that this was by no means the case. It appeared probable, therefore, that from some disturbing cause the vortex would not form, or would only form imperfectly, behind the plate.

This view was strengthened when, on trying the resistance of a flat plate, it did not appear to diminish after the plate had been started.

Accidentally, however, it was found that if the float to which the plate was attached was started suddenly and then released, the float and plate would move on apparently without any resistance. And more than this, for if the float were suddenly arrested and released, it would take up its motion again, showing that it was the water behind that was carrying it on.

There was evidence therefore of a vortex behind the disc. In the hope of rendering this motion visible, coloured water was injected in the neighbourhood of the disc, and then a beautiful vortex ring, exactly resembling the smoke ring, was seen to form behind the disc. If the float were released in time, this ring would carry the disc on with it; but if the speed of the disc were maintained uniform, the ring gradually dropped behind and broke up. Here then was another part played by the vortex previously undreamt of.

That the vortex takes a systematic part in almost every form of fluid motion was now evident. Any irregular solid moving through the water must from its angles send off lines of vortices such as those behind the oblique vane. As we move about we must be continually causing vortex rings and vortex bands in the air. Most of these will probably be irregular, and resemble more the curls in a smoke cloud than systematic rings. But from our mouths as we talk we must produce numberless rings.

One way in which rings are produced in perhaps as great numbers as from our mouths is by drops falling into the sea. If we colour the surface of a glass vessel full of water, and then let drops fall into it, rings are produced, which descend sometimes as much as two or three feet.

But the most striking rings are those produced in water, in a manner similar to that in which the smoke rings are produced, using coloured water instead of smoky air.

These rings are much more definite than smoke rings, and although they cannot move with higher velocities, since that of the smoke ring is unlimited, the speed at which they move is much more surprising.

In the air we are accustomed to see objects in rapid motion, and so far as our own notions are concerned, we are unaware of any resistance; but this is quite otherwise in water. Every swimmer knows what resistance water offers to his motions, so that when we see these rings flash through the water we cannot but be surprised. Yet a still more striking spectacle may be shown, if, instead of coloured water, a few bubbles of air be injected into the box from which the puff is sent; a beautiful ring of air is seen to shoot along through the water,

showing, like the lines of air behind the oblique vane, little or no tendency to rise to the surface.

Such is the ease with which these vortex rings in water move, and so slight is the disturbance which they cause in the water behind them, as to lead to the conclusion that they experience no resistance whatever, except perhaps a little caused by slight irregularities in their construction. Their velocity gradually diminishes; but this would appear to be accounted for by their growth in size, for they are thus continually taking up fresh water into their constitution, with which they have to share their velocity. Careful experiments have confirmed this view. It is found that the force of the blow they will strike is nearly independent of the distance of the object struck from the orifice.

The discovery of the ring behind the disc afforded the opportunity of observing the characteristics of these rings much better than was afforded by the smoke rings; and also suggested facts which had previously been overlooked. The manner of motion of the water which formed the ring and of the surrounding water was very clearly seen. It was at once seen that the visible ring, whether of coloured water or air, was merely the central line of the vortex; that it was surrounded by a mass of coloured water, bearing something the same proportion to the visible ring as a ball made by wrapping string (in and out) round a curtain ring until the aperture was entirely filled up. The disc, when it was there, formed the front of this ball or spheroid of water, but the rest of the surface of the ball had nothing to separate it from the surrounding water but its own integrity. Yet when the motion was very steady the surface of the ball was definite, and the entire moving mass might be rendered visible by colour. The water within the ball was everywhere gyrating round the central ring, as if the coils of string were each spinning round the curtain ring as an axis, the water moving forwards through the interior of the ring and backwards round the outside, the velocity of gyration gradually diminishing as the distance from the central ring is increased.

The way in which the water moves to let the ball pass can also be seen, either by streaking the water with colour or suspending small balls in it. In moving to get out of the way and let the ball of water pass, the surrounding water partakes as it were of the gyrating motion of the water within the *ball*, the particles moving in a horse-shoe fashion, so that at the actual surface of the *ball* the motion of the water outside is identical with that within, and there was no rubbing at the surface, and consequently no friction.

The maintenance of the shape of the moving mass of water against the unequal pressure of the surrounding water as it is pushed out of the way is what renders the internal gyratory motion essential to a mass of fluid moving through a fluid. The centrifugal force of this gyratory motion is what balances the excess of pressure of the surrounding water in the front and rear of the ball, compared with what it is at the sides.

It is impossible to have a ring in which the gyratory motion is great, and the velocity of progression slow. As the one motion dies out so does the other, and any attempt to accelerate the velocity of the ring by urging forward the disc, invariably destroyed it.

The striking ease with which the vortex ring, or the disc with the vortex ring behind it, moves through the water, naturally raised the question as to why a solid should experience resistance. Could it be that there was something in the particular spheroidal shape of these balls of water which allowed them to move freely. To try this, a solid of the same shape as the fluid ball was constructed and floated after the same manner as the disc. But when this was set in motion, it stopped directly—it would not move at all. What was the cause of this resistance? Here were two objects of the same shape and weight, the one of which moved freely through the water, and the other experienced very great resistance. The only difference was in the nature of the surface. As already explained, there is no friction at the surface of the water, whereas there must be friction between the water and the solid. But it could be easily shown that the resistance of the solid is much greater than what is accounted for by its surface friction or skin resistance. The only other respect in which these two surfaces differ is that the one is flexible, while the other is rigid, and this seems to be the cause of the difference in resistance.

If ribbons be attached to the edge of the disc, these ribbons will envelope the ball of water which follows it, presenting a surface which may be much greater than that of the solid; and yet this, being a flexible surface, the resistance of the disc with the vortex behind it is not very much greater than it would be without the ribbons—nothing to be compared to that of the solid. —

Colouring the water behind the solid shows, that instead of passing through the water without disturbing it, there is very great disturbance in its wake. An interesting question is as to whether this disturbance originates with the motion of the solid, or only after the solid is in motion. This is settled by colouring the water immediately in front of the solid before it is started. Then on starting it the colour is seen to spread out in a film entirely over the surface of the solid, at first without the least disturbance, but this follows almost immediately.

Among the most striking features of the vortex rings, is their apparent elasticity. When disturbed they not only recover their shape, but vibrate about their mean position like an elastic solid. So much so, as to lead Sir William Thomson to the idea that the elasticity of solid matter must be due to its being composed of vortex rings.

But apart from such considerations, this vibration is interesting as showing that the only form of ring which can progress steadily is the circular. Two parallel bands, such as those which follow the oblique vane, could progress if they were infinitely long, but if not, they must be continually destroyed from the ends. Those which

follow the oblique vane are continually dying out at one end, and being formed again at the other.

If an oval ring be formed behind an oval plate, the more sharply curved parts travel faster than the flatter parts; and hence, unless the plate be removed, the ring breaks up. It is possible, however, to withdraw the plate, so as to leave the oval ring, which proceeds wriggling along each portion moving in a direction perpendicular to that in which it is curved, and with a velocity proportional to the sharpness of the curvature. So that not only does the ring continually change its shape, but one part is continually falling behind, and then overtaking the other.

These were some of the forms of fluid motion which imagination or reason had failed to show us, but which had been revealed by the simple process of colouring the water.

Now that we can see what we are about, mathematics can be most usefully applied; and it is expected that when these facts come to be considered by those best able to do so, the theory of fluid motion will be placed on the same footing as the other branches of applied mechanics.

[O. R.]

Friday, February 16, 1877.

SIR T. FREDERICK ELLIOT, K.C. M.G. Vice-President, in the Chair.

PROFESSOR FREDERICK GUTHRIE, F.R.S.

Solid Water.

WHEN, some months ago, I received, through your excellent Secretary, a notification of your wish that I should undertake one of these Friday evening discourses, I looked upon the invitation as a command: as a command, if for no other reason, because, for some years past, I have, through your courtesy, been privileged to participate between these walls in many a rare intellectual treat.

As I cast about for a suitable subject, I felt sure that, at your hands, I should not incur the charge of egoism if I brought before you, as briefly and simply as I could, the results of some experimental researches which for the last few years have engrossed my leisure time. And whatever hesitation I had in selecting a subject of this nature, has been obliterated by the feeling that what I have to speak of to-night illustrates a generalization which, I think, has not hitherto been enunciated with sufficient distinctness, but which may be maintained with great show of reason. I will not call it a law of nature, for they who use the term law in connection with natural phenomena are, I believe, neither sufficiently alive to the insignificance of law, nor to the omnipotence of nature. Let me therefore call what I mean by the more expressive, because more ambiguous, term "Generalization." It is this: "Substances which are most abundant are in their nature most exceptional." At once, among the elements we find that great trinity, oxygen, hydrogen, and nitrogen, standing as a group far removed from other elements, only to differ from one another by immeasurable intervals. The metal sodium, than which there is none more remarkable, is perhaps the most abundant; while the rarer metals, such as gold, platinum, osmium, iridium, &c., have many characteristics in common.

It will not do to push this proposition too far: for even as I spoke, instances have occurred to you, as they have to me, where the generalization appears at least to fail. If, however, I wished to adduce the strongest testimony in its favour, I should speak of water, a compound body, and of all compound bodies as simple as any, and

perhaps as abundant. Let me glance at the properties which render it pre-eminent. Of all compound liquids, it has by far the greatest hardness or cohesion. Gather under like circumstances drops of water and of all other known liquids, and you will find those of water the largest. Endeavour to pass radiant heat through it, and you find it resists such passage with the greatest stubbornness: it is eminently athermanous. But compare its power of allowing heat of contact to pass through, and you find it to be by far the best liquid heat conductor. Examine its capacity for heat, and you find that it here exceeds all known liquids, with one exception, and that exception is a mixture containing a large proportion of water. Cast light on it, and it bends that light less than any substance, excepting its own offspring, ice. Finally, it enjoys that rare and almost unique property of having a state of maximum density at a temperature above its freezing point.

On all these grounds, the expression of the old Greek,

ἀριστον μὲν ὑδωρ,

seems to have been prophetic, if we understand *apistos* in its simple sense of pre-eminence.

I propose this evening to consider mainly one faculty of water, namely, its power of dissolving that innumerable class of bodies called salts, which may, I suppose, without much danger of a misunderstanding, be considered as bodies soluble in water, and which contain metals. I wish to consider the relationship between the water and the salt it has dissolved, and I desire to direct especial attention to the circumstances under which water becomes solid in presence of and in combination with other bodies.

Water may become solid in a variety of ways. First, by itself, losing heat, it becomes ice ; secondly, when thrown upon quick lime and similar bodies, by the loss of heat it becomes along with the lime a solid, slaked lime ; thirdly, if you pour water upon dried alum and similar bodies, and let the solution stand, you get dry crystals, I dare scarcely say containing water, but from which water can be readily got. Again, if you boil glue or isinglass with water, you get a more or less solid jelly, according to the quantity of water you employ.

These various ways by which water may be solidified result in the more or less complete obliteration of its character as water. Chemists tell us that in the slaking of lime we do not witness the mere juxtaposing of a molecule of water alongside a molecule of lime, but rather a double decomposition whereby the molecules of each constituent are decomposed and one or two new molecules are formed ; *

* Not $\text{CaO} + \text{HO} = \text{CaOHO}$, but $\text{Ca}_2\text{O} + \text{H}_2\text{O} = 2\text{CaHO}$,
 (Ca = 20, H = 1, O = 8) (Ca = 20, H = 1, O = 16)
 or $\text{CaO} + \text{H}_2\text{O} = \text{Ca}_2\text{HO}$.
 (Ca = 40, H = 1, O = 16)

and that when by heat the water from slaked lime is recovered, recomposition of quick lime and of water ensues. Far less violent is the action when burnt alum dissolves in water, and far more readily are the two again separated: while from the ordinary "washing soda" in moderately dry air the water gradually escapes by diffusion into the air. Yet in all these cases the water is held by the solid with some strength. Lastly, when glue or gum dissolves in water there appears to be no energy expended in the act of solution, they mix even as two gases mix.

Strictly speaking, when a grain of salt dissolves in a gallon of water both are destroyed; the salt ceases to be salt and the water ceases to be water: the two form a salt solution. This fact must never be forgotten, but its strict observance would land us here in the cumbersome restriction of denying the name of water to the liquids of our springs, rivers, and seas.

On the table you see examples of the various kinds of solid water. And first stands ice. In this room it is unnecessary for me to speak especially of this substance, which has formed for you the basis of so many an eloquent discourse. Again, there is water of combination, of constitution, of gelatinization, and of crystallization.

It is to be remarked, and is indeed for our present purpose most noteworthy, that whole classes of salts are known which solidify with water of crystallization, while others of no noticeable chemical difference reject water as they build themselves together. Nay, more, that salts most closely allied to one another in their chemical nature combine with water of crystallization in very different proportions. What is there peculiar in saltpeter, in lunar caustic, in sal-ammoniac, that they should hitherto have refused to associate themselves as solids with water; while alum, soda, and the "vitriols," white, green, and blue, combine with water and form crystals of such beauty; to me of such extreme interest because in their faces and edges, as in those of other and anhydrous crystals, nature for once makes use of planes and straight lines?

It has been my good fortune to have been able, to some extent, to wipe out this line of demarcation, to establish continuity; to prove, in short, that all salts whatever, which are soluble in water, are able to combine with it in definite weight-ratio to form solid crystalline bodies. I do not doubt but that we may consider the number of known definite compounds to have been thereby at least doubled.

The formation of these new solid water-compounds may perhaps be best approached by studying the phenomena which take place when any salt solution is cooled. Let us consider a boiling saturated solution of saltpeter. Take it from over the lamp, and let it cool. A certain quantity of the salt separates out, but the crystals are free from water. Cool it down to 0° C., more anhydrous saltpeter separates; but at 0° C. it is still rich in saltpeter, and is, of course, saturated at that temperature. What takes place if we go on cooling

below 0°C .? If pure anhydrous saltpeter were to go on separating out until it were all out, there would be left at some temperature below 0°C . pure liquid water—an impossibility. If, on the other hand, only pure ice were to separate out, we should get at last anhydrous saltpeter liquid below 0°C .: this is equally impossible. What actually does occur is this—anhydrous saltpeter goes on separating out until the solution has acquired a certain degree of weakness (11.20 per cent.), and this stage is reached at a certain temperature below 0°C . (-2.6). When still more heat is withdrawn, the temperature refuses to sink further, and the remainder of the solution begins to solidify, and continues to solidify at the temperature and with the composition it has reached until the last drop is solidified.

If, again, we begin with a very dilute solution of saltpeter, say one containing 2 oz. of saltpeter in 98 oz. of water, it is well known that such a solution requires to be cooled below the freezing point of water before solidification begins; and the differences of opinion which have prevailed as to whether pure ice or “impure” ice is separated in such cases arise apparently from the circumstance that solutions of different strength have been examined. From our solution, pure ice is separated at a little below 0°C . And as the temperature falls, more and more ice separates out, thus enriching the remaining solution. But this cannot go on indefinitely, for if it did so we should have at last anhydrous saltpeter liquid at some temperature below 0°C . The enrichment goes on as the temperature falls, until the same temperature and the same composition are reached as were reached in the case of the impoverishment of the saturated solution by the withdrawal of the saltpeter. And now again the temperature ceases to fall, the salt solution ceases to change its composition, the water and saltpeter solidify together at the same temperature and in the same ratio as they did before, until the last drop is solid.

What manner of body is this which is thus formed? A solid, of crystalline form, consisting of water and saltpeter in fixed ratio, and of constant freezing and melting points. A hydrate obviously, and because it can only exist in the solid form below the freezing point of water, we may call it a cryohydrate.

Thirty or forty of the most familiar soluble salts have been examined in a similar manner and with similar results. Each combine with a certain proportion of water at a certain temperature below zero C. The proportions are different with different salts, and so are the temperatures of solidification, and at present I can only see indications in a few cases of generalizations connecting the chemical compositions with the temperatures.

The Table A and Diagram B now nearly completely explain themselves.

TABLE A.—Shows (1) The CHEMICAL FORMULA of the SALT; (2) The LOWEST TEMPERATURE to be got by mixing the SALT with ICE; (3) TEMPERATURE of SOLIDIFICATION of the CRYOHYDRATE; (4) MOLECULAR RATIO between ANHYDROUS SALT and WATER of its CRYOHYDRATE (Water-worth); (5) PERCENTAGE of ANHYDROUS SALT in CRYOHYDRATE.

(1) Formula of Salt	(2) Temperature of Cryogen	(3) Temperature of Solidification of Cryohydrate.	(4) Molecular Ratio or Water-worth	(5) Percentage of Anhydrous Salt in Cryohydrate.
	°	°		
CaCl_2	- 33	- 37	11·8	36·45
NaBr	- 28	- 24	8·1	41·33
NH_4I	- 27	- 27·5	6·4	55·49
NaI	- 26·5	- 28	5·8	59·45
KI	- 22	- 22	8·5	52·07
NaCl	- 22	- 22	10·5	23·60
$\text{SrCl}_2 + 6\text{H}_2\text{O}$	- 18	- 17	22·9	27·57
NH_4^2SO_4	- 17·5	- 17	10·2	41·70
NH_4Br	- 17	- 17	11·1	32·12
NH_4NO_3	- 17	- 17·2	5·72	43·71
NaNO_3	- 16·5	- 17·5	8·13	40·80
NH_4Cl	- 16	- 15	12·4	19·27
KBr	- 13	- 13	13·94	32·15
KCl	- 10·5	- 11·4	16·61	20·03
K_2CrO_4	- 10·2	- 12	18·8	36·27
$\text{BaCl}_2 + 2\text{H}_2\text{O}$	- 7·2	- 8	37·8	23·2
AgNO_3	- 6·5	- 6·5	10·09	48·38
Sr_2NO_3	- 6	- 6	33·5	25·99
$\text{MgSO}_4 + 7\text{H}_2\text{O}$	- 5·3	- 5	23·8	21·86
$\text{ZnSO}_4 + 7\text{H}_2\text{O}$	- 5	- 7	20·0	30·84
KNO_3	- 3	- 2·6	44·6	11·20
Na_2CO_3	- 2·2	- 2	92·75	5·97
$\text{CuSO}_4 + 5\text{H}_2\text{O}$	- 2	- 2	43·7	16·89
$\text{FeSO}_4 + 7\text{H}_2\text{O}$	- 1·7	- 2·2	41·41	16·92
K_2SO_4	- 1·5	- 1·2	114·2	7·80
$\text{K}_2\text{Cr}_2\text{O}_7$	- 1	- 1	292·0	5·30
Ba_2NO_3	- 0·9	- 0·8	259·0	5·30
$\text{Na}_2\text{SO}_4 + 10\text{H}_2\text{O}$	- 0·7	- 0·7	165·6	4·55
KClO_3	- 0·7	- 0·5	222·0	2·93
$\text{Al}_2\text{NH}_4^2\text{SO}_4 + 12\text{H}_2\text{O}$	- 0·4	- 0·2	261·4	4·7
HgCl_2	- 0·2	- 0·2	450·0	3·24

In Diagram B are shown, as well as the cryohydrates (which are the points of reflexure, or lowest points of each curve), the temperatures at which various salts of various strengths (*a* left-hand branches) give up ice and (*b* right-hand branches) give up salt.

Let me only remark concerning these ratios of Table A, that those bodies at the bottom of the list are nearly pure ice, and yet by the generalization of continuity they are bodies of similar composition to those at the top of the list which are well within the limits of chemical ratio. One is tempted to look upon these ratios as being brought about not by the same saturating capacity as determines

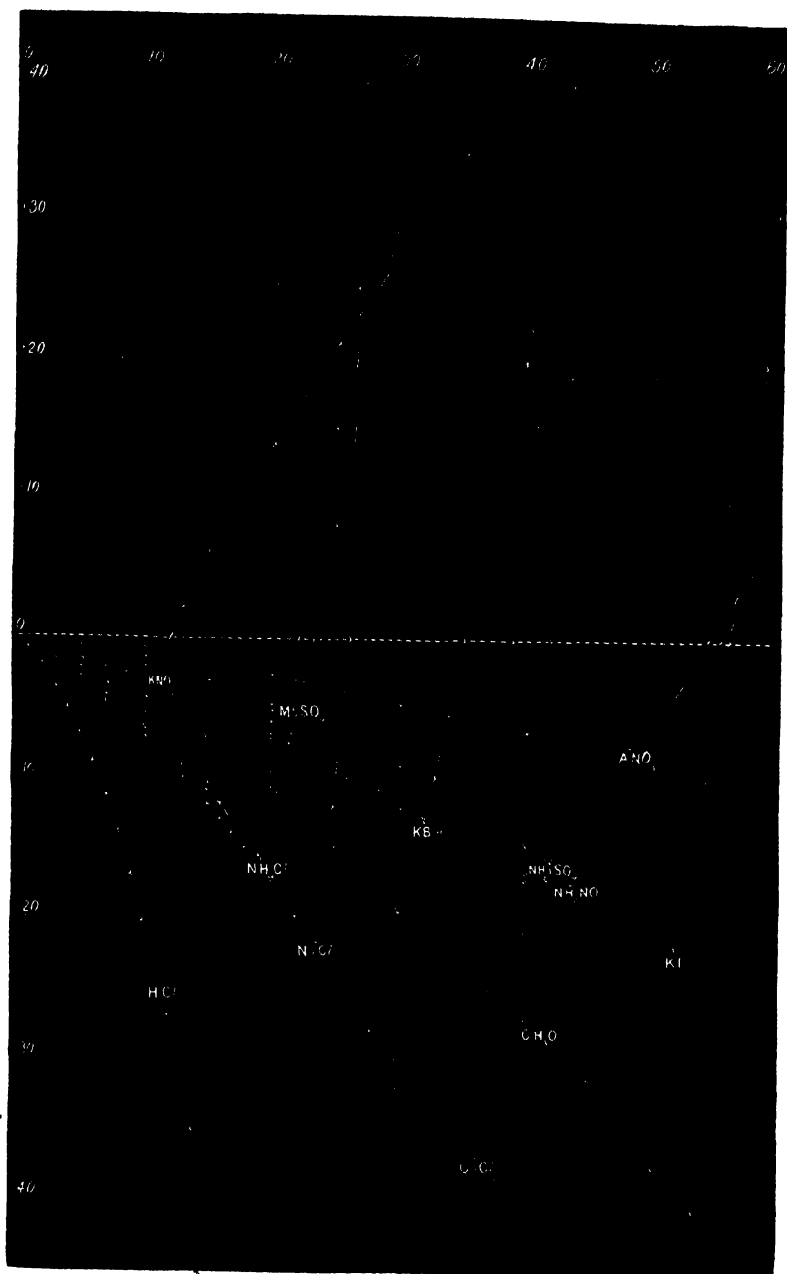


DIAGRAM B.

elementary union, but by a kind of crystallographic relationship, of which I can say no more because no more is known.

Very palpable evidence of what we may in this generation call physical relationship as distinguished from chemical relationship, is shown in the composition of innumerable minerals, and notably in the water quantity of various silicates, the composition of which can only be reconciled to ordinary chemical ratio by the greatest licence in arithmetical manipulation. I say, "in this generation," for haply the time practically predicted by Berthollet at the beginning of the century cannot be remote when the barrier between the two sciences will vanish.

Is it likely that so numerous and interesting a class of bodies as these cryohydrates should be mere creatures of the physical laboratory, and be without a function in nature? I trow not. They affect the composition of polar ice as follows.

Although sea water has no maximum density, and therefore ice can be formed anywhere in its mass, yet it loses heat mainly from the surface, and it is there that ice is chiefly formed. If the fall of temperature be gradual, the crystals of pure water which solidify are for the moment surrounded by cold sea water deprived of a portion of pure water, that is enriched sea water—a stronger brine. This sinks and diffuses, and gives place to fresher sea, which in its turn yields pure ice. By gravity and osmose, in time, the pure sea is renewed in the region of gelation, and pure ice results. But if the loss of heat be sudden and considerable, the salts of the sea are fixed as cryohydrates with the water, and so perpetuated *in situ* according to the temperature at which their cryohydrates solidify. And I should expect that paleocrystic ice formed from the freezing-sea would contain the metals sodium, magnesium, and calcium in a different relative proportion to that in which they exist in the sea water. Be this, however, as it may, it is clear to me that no theory of ocean circulation can be complete which does not take into account the formation of cryohydrates in the polar regions.

These compounds of salts with water have both a great use in many a familiar operation, and a great significance in many a familiar phenomenon. With regard to their use, I need only mention the fact, that it is clear that by their means we can attain to and maintain with absolute constancy many definite temperatures below 0° C. For a body plunged into a melting or solidifying cryohydrate will be maintained at a temperature as constant as that of melting ice or freezing water.

With regard to their significance, they give us a complete key to the hitherto closely concealed *rationale* of freezing mixtures or cryogenes made by mixing ice or snow with various salts. For the degree of cold which can be reached on mixing a salt with ice can never exceed in lowness the temperature at which the cryohydrate solidifies, because the consequent solidification of the cryohydrate would furnish heat. Nay, more. Since of all ratios between

the salt and the water that of the cryohydrate demands the lowest temperature for solidification, the liquid portion of a freezing mixture can neither be stronger nor weaker than the cryohydrate, it is the cryohydrate and the slightest further loss of heat causes solidification. Look now at columns (2) and (3) of Table A, and you see how closely parallel, how, indeed, within the limits of experimental error, identical are the two series of numbers.

By cooling a thick slab of glass in a freezing mixture, and dropping upon it various salt solutions, I show you now a few cryohydrates in the act of solidification.

I may mention that not only metallic salts, but crystalline solids, of organic and inorganic origin form similar cryohydrates. Amongst the most interesting of these are the cryohydrates of alcohol and ether. The latter contains a large proportion of water, and its temperature of solidification is so little below zero C. that I can show it you. Solidified in a test tube, and removed therefrom, it forms a white crystalline rod, like a candle. The ether burns away when a light is applied to one end, and, by its non-luminosity, clearly illustrates the generalization of Dr. Frankland, that, other things being the same, a cold combustible burns with less luminosity than a hot one.

Let me here turn for a moment to the comparison between the effects of heat and cold upon salt solutions, and notice how closely parallel are the two series of phenomena.

Compare the decomposition of a salt solution by the loss of heat with the decomposition by gain of heat when such a solution boils. And in instituting this comparison, we must bear in mind how much more sensitive to variation in pressure is the boiling than the solidifying point.

And before quitting this part of the subject, I may call to mind

(1) A solution poorer than the cryohydrate loses heat; ice is formed.

(2) This goes on until the proportion of the cryohydrate is reached, the temperature falling.

(3) The cryohydrate may be reached by freezing out ice from a weaker solution, or by any other withdrawal of water.

(4) When ice separates from a liquid, it remains in contact with the liquid, and endeavours to redissolve therein.

(5) When by the separation of ice the proportion of the cryohydrate is reached (nearly independent of pressure), ice and the salt separate simultaneously.

(1) A solution poorer than that saturated at a given temperature receives heat; vapour is formed.

(2) This goes on until saturation is reached, the temperature rising.

(3) Saturation may be reached by evaporation, boiling, or any other withdrawal of water.

(4) Vapour separated from a liquid is removed from the field of contention, unless the liquid be enclosed with the vapour.

(5) When by the separation of vapour the proportion of saturation is reached (very dependent upon pressure), vapour and the salt separate simultaneously.

(6) The two bodies (ice and the salt) being crystallizable solids, unite to form a crystallizable cryohydrate which exhibits a constant gravimetric composition.

(7) A cryohydrate in the act of solidification shows identity of composition between the solid and liquid portions. The temperature of solidification is constant.

(6) One being a solid and the other a vapour, they do not unite, but in their separation preserve a constant gravimetric ratio under like conditions of pressure.

(7) A saturated solution, when boiling, shows the same ratio between the vapour formed and the salt precipitated as exists between the liquid water present and the salt it holds in solution. The temperature of boiling is (under like pressure) constant.

the fact that we find amongst the phenomena of igneous fusion facts perfectly analogous with those which we have been studying. Thus, in Pattinson's process for the desilverizing of lead, the mass containing a small percentage of silver is melted and gradually cooled, lead (ice) separates out in almost perfect purity, the temperature sinks, and more and more lead is separated, until, as Dr. Percy informs me, a two and a quarter per cent. of silver lead alloy, a pyro-plumbide (a cryohydrate), is reached.

Lastly, let us reflect upon the solidification of water in jellies, and its attitude towards colloid bodies.

My illustrious teacher Graham, in a series of researches which have perhaps never been surpassed for philosophical insight, showed how all matter is divisible into two great classes, crystalloid and colloid. He proved that a crystalloid body penetrates through a colloid without essential obstruction. The colloid and crystalloid have no grip on one another. And quite in accordance with Graham's views I find that, although gum-arabic is far more soluble in water than table salt, we totally fail to make a freezing mixture with gum and ice or snow. And inversely, when a strong solution of gum or glue is cooled, the temperature cannot be brought below 0°C . until the whole of the water has been separated as ice. This being so, we ought also to find that the presence of gum or glue in water does not raise its boiling point, as do the presence of crystalline salts. Experiment shows us that the boiling point of water is really and considerably lowered, so that if, for instance, I remove the atmospheric pressure from two vessels slightly warmed, the one containing 50 per cent. of gum and the other pure water, the gum solution is the first to boil.

In the series of barometer tubes on the table, whose images I throw on the screen, you have (1) an ordinary barometer, (2) a similar barometer with a crystal of alum in the vacuum, (3) with a saturated solution of rock salt, (4) with water, (5) with a morsel of size, and (6) with a 50 per cent. solution of gum-arabic. It is observed that the depression of the mercury, which of course measures the vapour tension, is in the order mentioned. The solid water of crystallization leaves the alum, but is partly restrained by the affinity of the residue. The saturated salt solution again, but more feebly, restrains the

water, while the gum and size do not restrain the vapour tension of the water at all; they have no grip on the water.

Even through the colloid caoutchouc, of which the toy air-balls are made, water penetrates with marvellous facility. The one on the table, which weighs now about 700 grams, weighed 750 grams only a few weeks ago. It has been losing 0.06 grams per hour with remarkable regularity. And I suppose, if we could see the structure of a jelly, we should find it to consist of a network of solid fibres hampering the motion of the crystalloid liquid among them; or of cells of solid elastic matter, containing liquid such as the mass of cells on the table.

The hour is up, and I must end. My task will not have been essayed in vain if I have brought forward evidence that, in the philosophy of the simplest things, yet much remains to be disclosed. Far from me the thought of undervaluing the labours of those who from time to time enrich science with hundreds of new substances of complex composition. On the contrary, I admire, I am grateful to them for their successful efforts; for I am thoroughly assured that it is by the comparison of terms of series, which terms stand apart from one another by almost imperceptible differentials, that the great integral curves of natural generalizations can be traced out. And yet I say, and earnestly maintain, that in the philosophy of the most familiar properties of the most familiar things, there are, as it were, lying at our very doors, vast and unexplored regions; meads brightly blooming with the unplucked flowers, and orchards mellow with the ungarnered fruits of natural truth.

[F. G.]

Friday, February 23, 1877.

SIR W. FREDERICK POLLOCK, BART. M.A. Vice-President,
in the Chair.

JOHN FLETCHER MOULTON, Esq. M.R.I.

Matter and Ether.

ALL are familiar with the process by which the discovery of the laws that govern phenomena is effected. Close study of various instances of some one phenomenon, with their general likeness and their individual peculiarities, leads, either by the slow process of trial and error or by some happy guess, to the discovery of the law to which the observed variations all conform. When this is once ascertained, the whole group of phenomena fall into harmony, and instead of a mass of separate observations, science seems but the exemplification of a single law. This step in the simplification and unification of nature taken, the human mind is free to seek further conquests. But great as is the advance made by such a step, the mind cannot rest content with it. The dry mathematical expressions which we know as the laws of nature, are soon felt to assuage scientific curiosity to a very imperfect degree. No sooner have we discovered the law that governs any set of phenomena, than we are irresistibly drawn to ask the question, How comes it that this is the governing law? of what set of hidden causes is it the outcome? And thus we are led to seek for the mechanism of nature and to find the physical causes of its laws. Nay, we go further; we cannot be content till we discover the nature and properties of the subject matter of its phenomena, and can deduce from these the previously discovered laws as necessary consequences. And the complete realization of one part, at least, of this search, is not beyond the bounds of possibility. It probably will some day be known to the human race that the whole of nature is but the manifestation of a very few distinct physical existences, possessed of known properties of so simple a kind and so universal in their presence that experience can never enable us to analyze them farther. The possible forms assumed by these elements will be deducible from their properties; and the more complex laws that will regulate the behaviour of the resulting substances, will be problems determinable from their known structure. Thus all nature will be theoretically the resultant of the interaction of known agencies, and the solution will be complete, even though the stupendous difficulties of the analysis

necessary to deduce the laws of even the more simple phenomena from the properties of these elements should compel the men of that far distant future to arrive at laws by induction from experiment, just as we do now already in the simplest of all sciences—astronomy. In this science, the phenomena of which are due to only four laws, each of which is capable of statement in most simple terms, the complexity of the analysis well-nigh drives astronomers to abandon calculation for observation, in the more delicate refinements of accuracy in which they indulge. Similar considerations will always operate to keep distinct the sciences that deal with distinct classes of phenomena, long after it has become a recognized truth that they are all the more or less complex manifestations of some few known elemental, physical existences. And certainly no considerations of the limits of possible success can avail to destroy the fascination of researches into the ultimate constitution of the existences of which nature is built up—the minute anatomy of the universe.

But although investigations of this nature are so interesting, and promise not only success, but success of the highest order, and although the interest of the research is common to the devotees of every science, inasmuch as it deals with that which underlies them all, it is most remarkable that so little advance has been made in this direction. And not only is it the case that we are compelled to admit that our ignorance of the ultimate constitution of matter is well-nigh as dense now as it ever was, but if we examine the attempts at solving the problem, hitherto made, they strike us at once as having the strangest characteristics. While in most of the other regions of research the results of all investigators have a certain family likeness, and the theories they propose—though perhaps mutually exclusive—have many points in common, yet here we find that the different solutions proposed have the wildest dissimilarity, and many of them present so fantastic an appearance, that it is difficult to believe that they are the productions of the sober investigators whose names they bear. We are too apt to pass lightly over the lesson taught us by the contemporaneous existence of the corpuscular and the undulatory theories of light. That two theories so diametrically opposite in nature, hypothesizing such utterly different constructions and properties of matter, could at a time not so very long past have been considered as possessing tolerably equal claims to acceptance, opens up a vista of ignorance as to the ultimate constitution of matter which is very humiliating. Nor will it suffice to say that those were the days when true science was in its infancy. Though the dispute between the two theories of light was speedily settled by the complete defeat of the corpuscular theory, and our ignorance of the real mechanism that produces and transmits light was rendered thereby less total—in fact we may say that it was so far dispelled that only those capable of thoroughly understanding the subject, can feel the difficulties and imperfections of the accepted theory—yet similar struggles are still going on in other kindred subjects, and for them

no such excuse can be pleaded. Take, for instance, electricity and magnetism. Our knowledge of their phenomena is extraordinarily wide; such a book as Wiedemann's 'Galvanismus' shows an accumulation of observations on one simple branch of the subject that can scarcely be paralleled in any other science. Yet if we look at the rival theories as to the nature of electricity, and its connection with matter, they seem so grotesque and so dissimilar—so like mere guesses in short—that we can scarcely help fancying that we are back in the days of Lucretius, when the best qualification for being a philosopher was to be an imaginative poet. And indeed in fertility of imagination, the authors of such theories as those to which we are referring seem not unworthy rivals of the Roman poet, and they make similar demands on our powers of belief. Weber and Ampère's ideas of magnetism being caused by each molecule of matter having its own special electric current circulating round it everlastingly; Poisson's idea that it is caused by each molecule being permeated by two mutually neutralizing fluids, capable of being separated by external attraction, but incapable of being removed from the molecule; the rival theories of two fluids, of one fluid, and of no fluid, in electricity, the numerous theories as to the nature of the luminiferous ether and its relation to matter, and the vortex theory of atoms, suffice to show that no effective check has as yet been placed on the free use of the imagination in this department of research, and seem to give some colour to the suggestion that the intolerance of credulity, professed by men of science, is easily relaxed by them in favour of their own pet theories.

The chief and immediate cause of this is not far to seek. Any attempt to arrive at the hidden mechanism which causes a phenomenon, must be a direct reflex of the knowledge and the ignorance of the age in which it is made. Let us take the case of some ingenious machine performing some known operations. If a person wholly ignorant of mechanism, save so far as the objects of common life teach it to intelligent observers, were to attempt to solve the problem of its construction, he would seek for some arrangement of levers or other mechanical appliances of the simplest and most elementary nature, which would give the desired result. If a mechanician were to apply himself to the same problem, he would have present to his mind all the refinements of mechanical science, and would probably arrive at a solution, no portion of which would resemble the one composed of the simpler elements, while his might in no respect resemble that which would be arrived at by one who, in addition to possessing a knowledge of mechanism, was also a skilled electrician. Each of the solutions would consist of the elements which the experience and knowledge of the maker enabled him to use, and there would be no probability of any of them representing the actual construction of the machine in question, unless the artifices used in its construction were such as were known to some of the persons who were thus attempting to reconstruct it. Just so is it with the attempts we make to arrive

at the mechanism of nature. They are charged to the full with our ignorance. If we happen to be acquainted with structure similar to the actual structure sought for, then success is possible, and some discoverer will in all probability arrive at a close approximation to the real state of things. If we do not, then all our efforts will but lead us to the discovery of a *possible* mechanism—one which might cause the phenomenon, but which is not the one which actually does cause it; and with this we must rest content, till in some way or other our knowledge of possible elements of construction is widened, when we may return again to the problem and find a new solution, which may in its turn have to be replaced by future ones. Take, for example, the question of the structure of matter. Matter was known to move with little or no resistance through the ether, to attract other matter, to be capable of great complexity in its nature, inasmuch as the light proceeding from elements, when in a state of incandescent gas, shows that they are capable of a large number of fundamental vibrations. To explain all this many most ingenious hypotheses were devised, both as to ether and matter; molecules or atoms were viewed as complex arrangements of parts vibrating or revolving under their mutual attractions. Ether was made an imponderable. Space was filled with ultra-mundane corpuscles, which, by their perpetual rain on all masses of solid matter, caused the phenomenon of gravitation. At length Helmholtz discovered vortex-motion. Vortex rings were found to move with little or no resistance in the medium, whether fluid or gaseous, in which they were formed; they were sensible of the presence of one another though not in contact, they were capable of being made to have the most intricate forms, and to take up the most complicated systems of vibrations. Instantly a vortex-theory of matter was devised, which has very much to recommend it, and which is at present the one in highest favour. But just as it was only rendered possible by Helmholtz's discovery of the new form of motion after which it is named, so it may in its turn have to give way to other theories which enlarged knowledge shall have enabled us to suggest.

The difficulty at once suggests itself, that if we admit that these theories as to the actual mechanism of nature are so intimately dependent on the state of the ignorance or knowledge in which we are when they are framed, how can it be right to attach any credence to them? How can we believe a theory at the same time that we admit that it will be probably displaced by another and a different one which will have at least as high claims to our belief? Science would at once lose all claim to be called the strictest school of belief, if it countenanced any such moral gymnastics as a belief which could thus co-exist with disbelief. And yet so great is the assistance derived from a well-constructed theory as to the mechanism producing phenomena, that she cannot afford to allow all efforts at solving such problems to be delayed until there comes a stage of such perfect knowledge, that the mind might claim to be capable of pronouncing on them with certainty—if indeed such a time could ever come. So she

boldly faces the difficulty of which we have spoken—the difficulty of showing any other choice open to scientific men, than either to be credulous or to be timid—by distinctly recognizing a class of scientific fictions, or, as they are usually called, hypotheses. These are theories as to the mechanism of nature which, either completely or to a great extent, account for some set of phenomena, and which therefore, so far as our knowledge goes, may correctly describe the whole or some part of the actual cause of the phenomena, i. e. the mechanism that produces them.

Nothing is more important in scientific thought than to distinguish between these hypotheses and laws. The discoverer of laws has nothing to do with actual causes. He only notices and formulates connections and relations between phenomena, and these formulations are laws. So far as the law is concerned, it is immaterial whether the one of two connected phenomena is the cause or the effect of the other, or whether the relation between them arises from their being both connected with a third phenomenon; the law is equally true in all cases. So long as the induction which has led to it has been duly and carefully performed, it is true and will never be displaced or superseded, however mistaken were the ideas which its framer possessed of the nature or causes of the phenomena to which it relates. Newton was quite right when he said, *hypotheses non fingo*; for the portion of his great achievements to which he was referring consisted in the demonstration of the existence of certain laws, and not in the explanation of their causes. But he, as well as all other great men of science, when the right time came, was ready to frame hypotheses, to start these scientific fictions, which were to be thankfully received, studied, tested, respected, worked from, and in short, everything but actually believed in. And he least of all would have, on the one hand, despised these tentative solutions, or, on the other hand, lightly believed in their truth. The whole of his work shows that he appreciated the full value of hypotheses, a value which it is difficult to express clearly, but which every learner or teacher of science feels only too keenly. For, without some guiding idea as to the nature and causes of phenomena, the mind is very sluggish in devising good methods of investigation; but so soon as a good hypothesis has been formed, it is so suggestive of fields of research and of experiments, that, whether it be true or false, there follows an immediate and rapid increase of knowledge. For a hypothesis may be a good one without being a true one. It may render the greatest assistance to the mind, it may be so well chosen that it accounts for kindred phenomena, not known at the time when it was first suggested, it may lead to the discovery of new laws, and it may enable calculations to be made which are of the highest value; and yet it may turn out to be radically false. Even the theory that heat was an imponderable fluid, might put forth a strong claim to our gratitude for the assistance it gave to early discoveries. To be thus useful for a time, it is not necessary that the assigned mechanism should be the

true one, but only that the laws that result from its structure should closely correspond with the more potent of the laws that actually direct the observed phenomena. And just as this is all that a hypothesis need do, so is it all that its success entitles us to believe that it is doing; and the true scientific attitude of mind towards hypotheses is to recognize them as describing causes which would produce results similar to those observed, and which, if not truly representing the mechanism which actually causes the results, at all events would produce results governed by the same laws.

How then are we to take the further step of selecting from amongst those rival hypotheses, each of which professes to give some mechanism able to produce a particular set of phenomena, the one that actually represents the mechanism by which the phenomena are in fact produced? This is the most serious and the most difficult step in discovery. And yet, at first sight, considering how complex are the phenomena that have to be explained, it would seem that any theory that succeeded in accounting for even a portion of them must be very near to the truth; and it is so usual to consider that this is the final and sufficient test of the claims of a hypothesis, viz. that it should suffice to account for the phenomena, that when they are very complex it is often considered a more than sufficient test, and the hypothesis is accepted in spite of its being in many respects undeniably deficient. But, in fact, so soon as we begin to apply ourselves seriously to the problems of the constitution of matter—the hidden mechanism of nature—we are forced to abandon in great measure all such ideas. For we find that we have no true measure of complexity. From one single simple law will follow the most various and complex results, and hence any mechanism so designed as to exemplify in its results the working of that single law would, under such a canon as the one just referred to, be able to claim as evidence of its truth all the complexity which follows from that law. Yet such evidence would equally avail to support the claims of any other mechanism, whose results similarly obeyed that law, and of such mechanisms there might be many. This has been often exemplified in the history of science. The truth of a hypothesis has appeared to be sufficiently demonstrated by the manner in which it fully accounted for complex phenomena, and it has been accepted as a physical truth on such grounds, until some other hypothesis has been shown equally capable of accounting for them; and the success of both has been subsequently traced to their alike leading to results that were obedient to some one fundamental law, to the working of which the whole of the observed complexity was due. In the history of such deep-reaching principles as that of the Conservation of Energy this has been a common occurrence; but other instances are not wanting. After Sir W. R. Hamilton had deduced theoretically from Fresnel's Theory of Light, that in biaxal crystals there must be internal and external conical refraction, and their existence had been thereupon experimentally demonstrated by Dr. Lloyd, one might well have fancied that the accuracy of so remarkable a prognostication was sufficient

to establish Fresnel's Theory in all its details. Yet a theory framed by Cauchy, which, though in many respects similar to Fresnel's Theory, is yet in fact wholly irreconcilable with it, was subsequently found to account equally for the phenomena; and it is probable that any theory of undulatory transmission in a non-isotropic medium might be made to do the like. In fact, we can express in abstract language the weakness of the canon which would make the acceptance of a theory follow from its success in explaining complex phenomena, by saying that to render the canon a good one, complexity must be measured, not by the apparent intricacy of the resulting phenomena, or the apparent difficulty of accounting for them, but by the number of independent laws by which the phenomena are governed, and which are successfully accounted for by the proposed mechanism. And as we are seldom in a position to pronounce on the question of the independence of the laws that govern a set of phenomena, i.e. as to whether they are all traceable to a very few fundamental laws or not, we are seldom able to estimate the complexity of those phenomena in the way that would alone justify us in taking it as sufficient warrant for the acceptance of a successful hypothesis.

Nor is this the only one of the well-tried and approved canons of discovery that fails us when we are engaged in researches in the unknown land of the ultimate constitution of that of which the universe is composed. There is no principle which is more constantly present to the mind of the scientific investigator in his search for the causes of phenomena than that of simplicity. Wondrously complex as are the processes that are going on all around us in nature—so apparently complex that the untaught mind has in all ages sought to ascribe them, in a greater or less degree, to consciousness and volition resident in the things themselves, or in beings possessing the power to direct them—science has so often found that these highly complex results come from the very simplest causes, that the investigator expects to find simplicity in his results, and naturally inclines to believe that explanation to be the true one which accounts in the most simple manner for the observed phenomena. This has been advanced by some persons almost to the dignity of a law of thought, and the mind is considered by them to be constrained to believe in the truth of the simplest hypothesis that explains a set of phenomena to the exclusion of all more complex ones.

It is not very easy satisfactorily to account for the undoubted value of this canon, viz. that the simplest hypothesis is probably the true one. That there can be any truth in it in its abstract form (as is generally understood) is not probable. There is no reason to think that nature has any preference for simplicity over complexity, if indeed it is possible to attach any meaning to such phrases. The deeper our knowledge becomes, the greater the complexity that confronts us, and the fainter our hope of finding that the ultimate solution will be a simple one. It is probable that much of the value of the canon arises from the fact that the simpler hypothesis will in general be the one that supposes the concurrent action of the fewest

independent causes ; and it is, of course, more probable that a smaller number of independent causes should co-operate than that a larger number should do so. But the value of the canon mainly lies in the view which the mind instinctively takes of simplicity. That is to us simple which is the result of means and processes to which we are thoroughly accustomed, and with the results of which we are fully familiar. Operations the most complex in their nature are often felt to be simple, and scarcely to need any explanation, solely because they are so common. It seems, for instance, almost superfluous to invent elaborate mechanism to account for such simple phenomena as evaporation or weight. And thus a hypothesis which is felt to be simple is usually one which traces the phenomena to the action of causes with which we are very familiar, i. e. which are constantly at work around us, and which are therefore just the causes that are the most probable.

From such considerations we at once see how useless must the canon of simplicity be to us when investigating the ultimate constitution of the materials of which the universe is built up. For, in the first place, we have little or nothing to guide us as to the probability of the concurrence of different causes in this unknown region, and secondly, a thing which is of infinitely greater moment, we are absolutely ignorant (save in one or two isolated points) of the types of structure and action that we may expect to find commonly exemplified therein. For in seeking to determine the ultimate constitution of matter and ether, and of all that directly or indirectly acts upon them, we are going beyond all the phenomena with which we have been rendered familiar by observation, whether general or special, and we are occupied in ascertaining the mechanism by which matter and ether are enabled to produce the phenomena we see. Now, of this we have no previous experience, and it cannot be too distinctly kept in mind that where there is no experience there is absolute ignorance. In the world around us we see only the aggregate results of infinitely numerous separate actions, none of which are simply cognizable by our senses or our instruments. Every experience of matter that we have in mechanics is of matter acting in masses. Chemistry and physics give us certain phenomena, caused doubtless by a more intimate action of matter upon matter, but the results are only known to us in gross ; and even if we assume that the process is uniform throughout, it is only the result of that process that we see, and its nature is wholly concealed from our view. Similar remarks apply to the other branches of science. Nowhere do we get any direct information as to the nature or details of these processes, or as to the mechanism by which they are rendered possible, and thus we nowhere get any knowledge of the types of mechanism that we may expect to find at work. It is true that in all action of matter upon matter we see that certain laws are universally obeyed. But all that this enables us confidently to enunciate is, that the nature of matter must be such that when matter acts upon matter in appreciable quantities, such and such laws obtain. We are not even justified in asserting that the most

universal of these laws must necessarily hold good in the case of the separate actions of which the aggregate is made up.* Still less are we in a position to say that one hypothesis is to be preferred to another, because it hypothesizes only such types of structure or action as we are familiar with in our experience of the world of visible phenomena. It is scarcely too much to say that at present our ignorance of the ultimate constitution of matter is such that no one suggested structure ought to be viewed by us as being in itself more simple or more probable than another.

Unable then to use those canons in their ordinary form, we are driven back to the truths that underlie them. It is true that we cannot rightly judge of the value of success in explaining the complex behaviour of matter as a test of the truth of a hypothesis. And it is also true that we cannot directly judge whether the causes we propose to assign for that behaviour are probable ones. But out of the combined effect of the two there arises a third canon of the highest value, specially adapted to meet the peculiar difficulties of the task. It may, perhaps, be expressed by saying that the probability of the truth of a suggested hypothesis, as to the constitution of matter or the nature and mode of transmission of its actions on other matter, is measured by the dissimilarity of the phenomena explained by it. So long as the hypothesis satisfactorily accounts for but one class of kindred phenomena, no matter how complex they may be and how satisfactorily it may account for them, its truth must still remain in doubt, inasmuch as from our ignorance we are unable to say how much is denoted by that success, in other words, how far such success may be due to these phenomena being necessary consequences of but very few laws, or even of a single one. But if the same hypothesis explains phenomena of a wholly different character to those which suggested it, and which so far as we can judge have no direct connection with them, then we are justified in accepting the hypothesis as a genuine contribution to our knowledge of nature.

This will be rendered clearer by an example. Take as an instance what is probably the most successful attempt that has yet been made to penetrate the darkness that surrounds the constitution of matter. Long ago, in order to explain the phenomena of combining proportions in chemistry, the hypothesis was framed that every element or chemical compound consisted of small atoms or molecules of definite size, constitution, and weight, and that the process of chemical combination consisted in the building up of new compound

* This is no idle refinement. No law would seem to be more absolutely without exception than that heat of itself tends to pass from a hot body to a cold body, i. e. that heat tends towards an equalization of temperature. Yet this has been shown to depend in some instances rather upon the law of averages than on the fundamental laws of energy, and to be inapplicable to the action of single molecules; and it is not impossible that we might be driven to take a similar view of such a law as that of the conservation of energy, though, fortunately, nothing as yet points to this, and it would, therefore, be unscientific to increase the difficulty of investigation by making such a hypothesis until it shall be found that there are good grounds for doing so.

molecules out of the molecules or atoms of the combining bodies, or the atoms that composed such molecules. The impetus given to the science of chemistry by this felicitous hypothesis can hardly be exaggerated. It permeated the whole of chemical research, and gradually came to be treated as though it represented a demonstrated fact. Against this the more accurate scientific thinkers protested, and were in the right in so doing. They pointed out that the only facts relating to the matter with which we were acquainted were those expressed by the law of combining proportions—that it was true that the atomic theory satisfactorily accounted for this law, but that the mere fact of its accounting for this single law was a very insufficient ground for accepting the absolute truth of the theory. There could be no doubt of the justness of these views, and the strictly hypothetical character of the theory was once more generally recognized. But of late the investigations of physicists into the dynamical theory of gases have shown that when substances are in the gaseous condition (in which alone the separate particles of which they are composed, are capable of free and independent motion, and — so to speak—of manifesting their separate constitution) they are composed of rapidly moving minute particles, of just such size and weight as the atomic theory would lead us to expect. Now this is precisely the type of confirmation which our canon points to as justifying belief. Nothing was farther from the thoughts of the inventor of the atomic theory than the explanation of the relations between temperature and pressure in gases—it was solely to account for a law of chemical combination that he framed his hypothesis—and yet we find that when in the state of gas the substances actually consist of just such particles as the atomic theory requires. No two more dissimilar classes of phenomena could well be imagined; and it is in consequence of this wide dissimilarity of the phenomena which it explains, that, although theories have been started in other branches of molecular physics which have successfully grappled with far more intricate phenomena, there is no theory of the ultimate constitution of matter which has nearly so high a claim to be regarded as an absolute physical truth as the atomic theory.

This canon seems to have but little connection with that of simplicity, or, as we may term it, the Law of Parsimony. And the reason of this is, as has been shown, that we are too deeply ignorant of the nature of the ultimate structure of any portion of the universe to be able to tell whether any suggested structure is a probable one, i. e. is one of a type frequently occurring. Slowly as we penetrate the mystery we shall acquire knowledge of particular instances or types of structure, and shall learn what sort of results to expect in our researches; and so soon as this stage is attained we shall rightly give weight to our inclination or repugnance towards any suggested hypothesis. But at present we are scarcely justified in doing so in any degree, and therefore it is of the greatest help to science that different investigators should separately work out theories depending some wholly on actions requiring a continuous medium for their

transmission, and others hypothesizing action at a distance. Such as succeed in explaining the phenomena to which they relate must, in the present state of things, be held to be of an equally hypothetical character, and, on the other hand, to be equally good candidates for final acceptance. As we have said, there is good reason to hope that this state of things is but temporary; but at present it exists, and it therefore profits nothing to turn the mind inward upon itself, to ask it to pronounce on the possibility or impossibility of things as to which it knows nothing. Nothing but laborious and prolonged experimental investigations will entitle us to give the preference to one or the other of the rival theories; and this will be due to the experience so gained, and not to any process depending on considerations of what is *à priori* possible or impossible in thought.

It is this utter absence of experience—this total ignorance of what is possible or impossible, probable or improbable—which causes us on the one hand to tolerate so kindly such fantastic hypotheses as those of which we have given instances in Weber's and Ampère's ideas as to molecules, or the collision theory of gravitation; and on the other hand to view with such doubt and suspicion, and to examine with such a jealous eye, the brilliant theories which have shed so much light on various parts of physics and chemistry. Take, for instance, the hypothesis of a luminiferous ether. In no branch of physics are the phenomena so striking as in physical optics, and no theory has ever fulfilled so difficult a task as has the Undulatory Theory in explaining and accounting for them; and yet if we deliberately consider the claims of this hypothesis to be regarded as a physical truth, we cannot free ourselves from the most serious and perplexing doubt. We must separate in our mind the laws of the Undulatory Theory from the mechanism by which the hypothesis seeks to account for them, and then if we weigh the evidence directly in favour of the existence of such a mechanism apart from such as is derived from its accounting for the laws of the Undulatory Theory, and when we contrast this with the enormous difficulty of reconciling the existence of such a mechanism with other phenomena, we are almost in despair. Remembering that light only makes itself known to us in connection with matter, the necessity of a hypothesis of so serious a character might well be doubted. If it were not for the finite velocity of light, and the great improbability (judging from our knowledge of the law and nature of energy) of there being a store of energy inherent in nothing for the time being, as there must be if the radiant light in the interplanetary spaces is not propagated through a continuous medium, it is very doubtful whether there would be any sufficient justification for the acceptance of the hypothesis of a luminiferous ether as being even a near approximation to a physical fact. At present the existence of a luminiferous ether is generally admitted, though it is very usual to doubt the existence of a medium for the transmission of electric action, and to look upon the latter class of phenomenon as an instance of action at a distance. Yet I doubt whether the evidence in favour of the existence of a luminiferous medium

differs at all in kind, or even greatly in degree, from that in favour of a medium for electric action; always supposing that it can be shown satisfactorily that induction across a vacuum occupies a finite time. If then we admit the existence of a luminiferous ether to be satisfactorily demonstrated, we must also admit the existence of an electric ether, and it will probably be found that other types of action have equal claims with these to special media for their transmission. Are we then to crowd space with interpenetrating media, each having as its sole function the transmission of some special kind of action? Without pronouncing dogmatically as to whether this can or cannot be the truth, it is clear that at present we are justified in declining to regard such conceptions as having any much higher rank than that of hypotheses judiciously framed for the purpose of simplifying our analysis, and assisting our thinking powers. If it should turn out that the so-called luminiferous ether accounts for the transmission of electric action, or—as at present seems more likely to be the case—that a medium hypothesized for the purpose of accounting for electric action is capable of satisfying all the needs of the Undulatory Theory of light, then indeed we may begin to think that our hypotheses closely represent physical facts. But such recognition is rightly withheld so long as each new hypothesis suffices only to explain the special type of phenomena for which it was framed.

Many of our best physicists are at work on such subjects as these, and are making good progress. Difficult as is the task, it is still one that occupies itself with what we have reason to believe is the simplest (if such a term can be appropriately used in such a connection), and the most uniform and homogeneous type of ultimate structure. Every glimpse that we get of the nature of matter (such, for instance, as the revelations of the spectroscope or the phenomena of crystallography and chemical change) makes us start back astonished at the well-nigh unimaginable complexity that it reveals. But in the case of light and electricity, although their manifestations must to some degree be bound up with matter, we have the attendant complexities of matter playing but a secondary part, and the main subject matter of the manifestations appears to be the result of some infinitely less complicated mechanism. It is true that we are at present baffled by this very difference from gross matter, which in all probability will ultimately render the problem more simple, inasmuch as our imagination is little rich in suggestions that rise above modified experience. But the fact remains that we are here brought most nearly face to face with the phenomena arising directly out of a comparatively simple type of ultimate constitution, and though the complex behaviour of matter would seem to give us more information as to its structure, and thus more guidance in our remarks, it is, as far as we can yet see, in the domain of light and electricity that we have best reason to expect success in our efforts to arrive at the hidden secrets of the mechanism of the universe.

[J. F. M.]

Friday, March 23, 1877.

WARREN DE LA RUE, Esq. D.C.L. F.R.S. in the Chair.

PROFESSOR J. H. GLADSTONE, Ph.D. F.R.S.

Influence of Chemical Constitution on the Refraction of Light.

THE object of the present discourse was to describe the advance that had been made in the subject of refraction equivalents since the lecture delivered on Friday, April 24, 1868. The speaker commenced by explaining the terms employed. The index of refraction of a body expresses the amount to which a ray of light is bent in passing from a vacuum into that body at any other than a right angle. It varies with the temperature, pressure, and every other condition which affects the volume of the substance. The specific refractive energy of a body is its refractive index minus unity, divided by the density, and this is a constant unaffected (or nearly so) by changes of temperature or pressure, passage from the solid to the liquid or gaseous condition, solution in other substances, or chemical combination within certain limits. The refraction equivalent is the specific refractive energy of a body multiplied by its chemical equivalent.

In the spring of 1868 the number of chemical elements of which the refraction equivalent had been determined with more or less accuracy was 17, a number which has since been increased to 52. The additions are principally the metals, and their refraction has been determined mainly from salts by taking advantage of the fact that a salt is not altered in specific refractive energy by solution in water or alcohol. About 200 salts have been examined, and by a comparison of the results the value of each constituent has been obtained.

The following table gives the complete list of the elements, and their optical properties, as far as they are known :—

Element	Atomic Weight	Refraction Equivalent	Specific Refractive Energy.
Aluminium	27·5	8·4	307
Antimony	122	24·5—31·8	201—260
Arsenic	75	15·4	205
Barium	137	15·8	115
Bismuth	210	39·3	187
Boron	11	4	364
Bromine	80	15·3—16·9	191—211
Cadmium	112	13·6	121
Cæsium	133	13·7 ?	103 ?
Calcium	40	10·4	260

Element.	Atomic Weight.	Refraction Equivalent	Specific Refractive Energy.
Carbon	12	5	416
Cerium	92	13·6 ?	148 ?
Chlorine	35·5	9·9—10·7	279—301
Chromium	52·2	15·9—23	305—438
Cobalt	58·8	10·8	184
Copper	63·5	11·6	183
Didymium	96	16	166
Fluorine	19	1·1 ?	73 ?
Gallium
Glucinum	9·3	5·6	606
Gold	196·7	21	122
Hydrogen	1	1·3—3·5	1·300—3·500
Indium	71
Iodine	127	24·5—27·2	193—214
Iridium	198	31·7 ?	160
Iron	56	12·0—20·1	214—359
Lanthanum	92	15·8	168
Lead	207	21·8	120
Lithium	7	3·8	540
Magnesium	24	7	292
Manganese	55	12·2—26·2	222—176
Mercury	200	21·3—29·0	107—145
Molybdenum	92
Nickel	58·8	10·4	177
Niobium	97·6
Nitrogen	14	1·1—5·3	293—378
Osmium	199
Oxygen	16	2·9	181
Palladium	106·5	22·2	208
Phosphorus	31	18·3	590
Platinum	197·4	26	132
Potassium	39·1	8·1	207
Rhodium	104	24·2 ?	232 ?
Rubidium	85·5	11	161
Ruthenium	101
Selenium	79	30·5	385
Silicon	28	7·4—6·8	263—238
Silver	108	13·5	125
Sodium	23	4·8	209
Strontium	87·5	13·6	155
Sulphur	32	16	500
Tantalum	137·5
Tellurium	128
Thallium	201	21·6	106
Thorium	231·5
Tin	118	27·0—19·2	203—162
Titanium	50	25·6	512
Tungsten	184
Uranium	120	10·8	90
Vanadium	51·2	25·3 ?	494 ?
Yttrium	68
Zinc	65	10·2	156
Zirconium	90	22·3	249

The sign ? indicates that the values have been deduced from only one compound, or that the different determinations are not fairly accordant

A glance at the above table reveals several remarkable features. It is evident, for instance, that such non-metallic elements as phosphorus, sulphur, selenium, carbon and boron have remarkably high specific refraction, while hydrogen is more than double any other in value. A more remarkable relation is one that appears when the specific refractive energy of the metals is compared with their combining proportion, that is to say, with the absolute amount which unites with one univalent atom—say 35·5 parts of chlorine—to form a stable compound. This is exhibited in the following table, in which the metals are ranged according to their combining proportions, hydrogen being included on chemical grounds.

Element	Specific Refractive Energy.	Combining Proportion.
Hydrogen	1·300	1
Glucinum	606	4·7
Lithium	540	7
Aluminium	307	9·1
Chromium	305	17·4
Magnesium	292	12
Calcium	260	20
Zirconium	219	22·4
Rhodium	232 ?	34·8
Manganese	222	27·5
Iron	214	28
Sodium	209	23
Palladium	208	26·6
Potassium	207	39·1
Arsenic	205	25
Tin	203	29·5
Antimony	201	24
Bismuth	187	69
Cobalt	181	29·4
Copper	183	31·7
Nickel	177	29·4
Didymium	166	48
Rubidium	164	42·7
Iridium	160 ?	49·5
Zinc	156	32·6
Strontium	155	43·8
Cerium	148	46
Platinum	132	49·3
Silver	125	108
Gold	122	65·7
Cadmium	121	56
Lead	120	103·5
Barium	115	68·5
Mercury	107	100
Thallium	106	204
Cæsium	103 ?	133
Uranium	90	120

It is evident that as the figures in the first column decrease, those in the second, as a rule, increase; that is to say, that the specific

refractive energy of a metal is inversely as its combining proportion, or, in other words, that those metals which have the greatest power in retarding the passage of a ray of light, are those which have the greatest power of saturating another element.

This law does not hold good absolutely: thus potassium and sodium, which have very different combining proportions—39·1 and 23 respectively—have practically the same refraction.

The extent of these discrepancies would be better seen if the above table were represented graphically. It would then appear as if there were a tendency to form not one curve, so much as three or four nearly concurrent curves, according to the particular character of the elements: thus the univalent metals, lithium, potassium, rubidium, silver, cesium and thallium, would seem to form a curve somewhat within the others.

These two properties—the saturating power and the refractive energy—are not directly proportional. It would rather appear that the specific refractive energy is inversely as the square root of the combining proportion. Thus for the univalent metals:—

Metal.	Specific Refractive Energy	Square Root of Combining Proportion	Product of these two Numbers
Hydrogen	1·300	1	1·3
Lithium	540	2·6	1·4
Sodium	209	4·8	1·0
Potassium	207	6·2	1·28
Rubidium	164	9·2	1·5
Silver	125	10·4	1·3
Cesium	103 ?	11·5	1·18 ?
Thallium	106	14·3	1·51

The law evidently holds true, roughly, for this group, with the exception of sodium, which as noticed above is discrepant. This is the more remarkable, as the group includes the elements of the highest and the lowest saturating power.

Another point in regard to which an advance has been made, is the following. If an element always had the same refractive energy in whatever way it was combined, we should be able to calculate beforehand the refraction equivalent of any compound of which the composition was known, and its refractive index also if we knew its density. This would be interesting, but we should evidently gain no information as to the chemical constitution or structure of the compound. But the fact is otherwise. As a rule, the refraction does not vary: carbon, for instance, whether alone as in the diamond, or combined in such diversified bodies as bisulphide of carbon, coal gas, cyanogen, alcohol, paraffin, sugar, and a hundred others, is exerting the same influence on the rays of light which traverse it; but there are certain compounds of carbon, in which it exerts a different influ-

ence, and it is from the consideration of this property—a wholly independent means—that we are able to confirm, or otherwise, our theoretical views of their constitution. This may be illustrated by the simpler case of iron. It is well known that one atom of iron will combine with either two or three univalent atoms, forming two classes of salts, which are totally distinct. Now in the ferrous salts, such as FeCl_2 , that have been examined, the refraction equivalent is 12.0, while in the ferric salts, as FeCl_3 , it is 20.1.

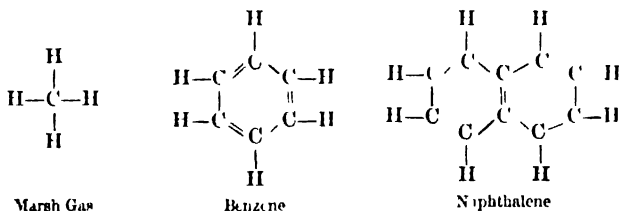
To return to carbon. It is well known that one atom of this element usually combines with four univalent atoms or radicles such as H . Cl . HO . NO_2 . CH_3 , or two divalent atoms such as O . S . In the immense multitude of carbon compounds of this order, the carbon is invariably found to have a refraction equivalent of 5.0. This is independent of the manner of combination, so that isomers such as chloride of ethylene and chloride of ethylidene have precisely the same value.

There is, however, a large group of bodies, in which the carbon is not saturated in the same way, but we are obliged to imagine that six atoms are associated together in each molecule, and that they thus combine with six univalent atoms. This large group forms what chemists call the aromatic group, of which benzene, aniline, oil of bitter almonds, benzoic acid, carbolic acid, are well-known members.

To the mind of the chemist, there is a very wide distinction in the fundamental constitution of these two classes of carbon compounds. The refraction goniometer exhibits this wide distinction in another way, for every member of this aromatic group which has been examined gives a value 6 or 7 above that which it would be if calculated on the supposition that carbon equals 5.

The naphthalene group has evidently a very different ultimate molecular structure, in which ten atoms of carbon are supposed to be associated. The refraction is 14 or 15 higher than the amount calculated from the value already given.

These three groups are typically expressed :—



Anthracene is probably more complicated, and its refraction exceeds the theoretical amount by a still larger quantity. In fact, refraction and dispersion increase very rapidly with the number of atoms of carbon that are not combined with at least two of hydrogen or their equivalent.

It is evident that this may afford a means of determining to what group a doubtful body may belong. Thus a colourless oily body, with a pleasant odour, named furfural, has been obtained from bran. The proportions of the elements are $C_5H_4O_2$, but it was quite a matter of opinion whether the five atoms of carbon were combined as above with H and O counting for eight, and therefore that furfural was analogous in constitution to the essential oils ($C_{11}H_{16}$ or $C_{11}H_{14}$), or whether it contained two of hydroxyl, HO, in which case it would be more analogous to the aromatic group, since there would be five carbon atoms to four univalent radicles, like benzene C_6H_6 , minus CH_2 . Now, the refraction equivalent of furfural is 42.3, which differs from the calculated value by 6.3, about the same difference as we find in the aromatic group, and far exceeding that observed in the case of the essential oils.*

Besides determining in this way the class of bodies to which a substance belongs, it is also evident that the prism may throw light on the constitution of groups of complex isomers, and we may expect that its indications will in many ways have an important influence on the theoretical chemistry of the future.

[J. H. G.]

* Since this discourse was delivered I have learned that recent researches have shown chemical reasons for associating furfural with the benzene group

Friday, April 13, 1877.

GEORGE BUSK, Esq. F.R.S. Treasurer and Vice-President,
in the Chair.

WILLIAM SPOTTISWOODE, Esq. M.A. LL.D. Treas. R.S. Sec. R.I.

Experiments with a Great Induction Coil.

THE experiments shown in this discourse were in illustration of the power of an induction coil constructed for me by Mr. Apps, and described in full in the 'Philosophical Magazine' for January of this year. The following are, however, the particulars of its principal parts. The coil, as arranged on this occasion, has a core consisting of a bundle of iron wires, each $\cdot 032$ inch thick, and forming together a solid cylinder 44 inches in length, and 3.56 inches in diameter. Its weight is 67 lbs. The copper wire used in this primary is 660 yards in length, $\cdot 096$ inch in diameter, has a conductivity of 93 per cent., and offers a total resistance of 2.3 ohms. It contains 1314 turns wound in six layers, has a total length of 42 inches, with an internal diameter of 3.75 inches, and an external of 4.75 inches. The total weight of this wire is 55 lbs.

The secondary consists of 280 miles of wire, forming a cylinder of 37.5 inches in length, 20 inches in external, and 9.5 inches in internal diameter. Its conductivity is 94 per cent., and its total resistance is equal to 110,200 ohms.

The condenser required for this coil proves to be much smaller than might have been at first expected. After a variety of experiments, it appeared that the most suitable size is that usually employed with a 10-inch spark coil, viz. 126 sheets of tinfoil 18 inches by 8.25, separated by two thicknesses of varnished paper, the two thicknesses measuring $\cdot 011$ inch.

When so arranged, this coil gave, with five quart cells of Grove, a spark of 28 inches; with ten similar cells, one of 33 inches; with thirty such cells, one of 37.5 inches, and subsequently one of 42 inches.

When the discharging points were placed about an inch apart, a flowing discharge was obtained, both at making and at breaking the

primary circuit. The sound which accompanies this discharge implies that it is intermittent.

With a 28-inch spark, produced by five quart cells, a block of flint glass 3 inches in thickness was pierced.

When a Leyden battery, having a coated surface of 10 feet, was inserted as a secondary condenser, the spark was sufficiently brilliant to allow its spectrum to be projected on a screen. In this spectrum the principal metallic lines were distinctly visible to the audience.

A Leyden battery, having a coated surface of 20 feet, was charged with 4 sparks from the coil.

In further exemplification of the power of this induction coil, some experiments were devised so as to exhibit to the audience effects previously observed only in a revolving mirror.

When, as is generally the case with an induction spark, the discharge occupies an appreciable interval of time, the image of it seen in a revolving mirror appears spread out to a breadth proportional to its duration, and to the velocity with which the mirror revolves. The successive phases of the phenomena are then arranged in successive positions, and may be studied separately, even when too rapid to be disentangled by the unassisted eye. This method, however, is adapted to only one or, at most, two observers at a time.

In experiments with luminous objects where there is sufficient brilliancy of light, the image as seen in a revolving mirror may be projected upon a screen by replacing the plane by a concave mirror of suitable focal length; but the comparative feebleness of light in vacuum tubes, even when illuminated by the great coil, rendered even this method inapplicable for the purposes of an audience. With a view to overcoming the difficulty, I next tried the effect of causing the tube itself to move during the discharge; and after a variety of experiments, I finally attached the tubes to the wooden arms about 6 feet in length, which were made to revolve about their centre like the arms of a windmill, and succeeded in exhibiting the phenomena on a large scale. The instrumental arrangements were in substance similar to those of a Gassiot's star; but the discharges, instead of being almost instantaneous, were of long duration; and instead of appearing as mere radii, they covered sectors of appreciable angle, sometimes semicircles, or even more, about the centre.

This being so, every stratification which remained fixed during the entire discharge described the arc of a circle, and a column of striæ appeared as a series of concentric luminous rings or portions of rings, according to the duration of the discharge. Similarly, striæ which were moving in one direction or another along the tube, described arcs of spirals, the pole of which was situated towards the beginning or end of the discharge, according as the motion was from the centre towards the extremities of the arms, or from the extremities towards the centre.

Any alteration in the velocity of the striæ along the tube, or

proper motion as I have termed it, was shown by a corresponding alteration in the curvature of the spiral; and any intermittence in the discharge by a dark sector in the field. In this manner the whole behaviour of the striæ during their brief period of existence was delineated on the screen.

The following are some of the general conclusions derived from the experiments repeated in this discourse.

I. The thin flake-like striæ, when sharp and well defined, are either short lived or have little proper motion, or both.

II. The apparent irregularity in the distribution of the striæ as seen by the eye, is due to their unequal duration, and to the various periods at which they are renewed.

III. The proper motion of the striæ is generally directed towards the positive terminal; and its velocity varies only within very narrow limits.

IV. Flocculent striæ, such as are usually seen in carbonic acid tubes, are a compound phenomenon; and are due to a succession of short-lived striæ which are regularly renewed. The positions at which the renewals take place determine the apparent proper motion of the flocculent striæ.

V. The velocity of proper motion varies, other circumstances being the same, with the diameter of the tube. This was notably exemplified in a conical tube.

VI. When the proper motion exceeds a certain limit, the striæ appear to the eye to be blended into an unbroken column of light, and all trace of stratification is lost. The mirror will in many cases resolve this column into its component striæ, but not in all.

The discharge from a Leyden jar, when sufficiently charged, is, as is well known, continuous through its entire length; but it still exhibits a dissymmetry in extending from the point of the positive to the hilt of the negative terminal. It is, moreover, so far as our present instrumental measurements extend, instantaneous, and cannot be spread out by a revolving mirror. Lastly, it exhibits no trace of stratification. This difference of effect appears to depend on that of tension. This was established by some experiments described in the 'Proceedings of the Royal Society,' 1877, vol. xxv. p. 73, and tend to show that this character of the jar discharge is due to tension.

A curious illustration of this was shown by inserting a Leyden jar in a loop circuit with the tube. By this means the current was divided; one part went to charge the jar, while the other part went directly through the tube. As long as the tension in the jar remained below a certain limit, the coil alone acted in the tube; but as soon as the charge in the jar was sufficient, it discharged itself through the tube. As seen in the mirror, the field of view showed first a stratified discharge, and then, following immediately upon it, a jar discharge or unbroken line of light.

It is, however, impossible to convey any adequate idea of these phenomena by mere description; and the reader who desires fuller

illustration of the subject is referred to the figures which accompany my paper in the 'Proceedings of the Royal Society,' 1877, vol. xxv. p. 73.

At the close of the discourse I expressed a hope that it might prove possible with this great coil to photograph the image of the phenomena here described; and I am glad to add that subsequent experience tends to confirm this hope.

[W. S.]

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